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A GUIDE TO THE SELECTION OF MATERIALS FOR MONITORING WELL CONSTRUCTION AND GROUND-WATER SAMPLING

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16. ABSTRACT

The project was initiated to supplement and update existing guidance documents for effective ground-water monitoring efforts. The areas of primary concern were the potential sources of errors in chemical analyses of subsurface samples caused by well construction and sampling materials, techniques or procedures. A critical review of the literature was conducted on various aspects of monitoring natural waters, materials' performance data and unpublished information on the success of various ground-water monitoring techniques. The results of the literature review were collected and reviewed by a panel of experts from government agencies, private hydrological consulting firms, the manufacturing industry and national standards organization. The publication consists of a thorough discussion of ground-water monitoring strategies, requirements and pitfalls. It concludes with a detailed treatment of the costs and benefits of recommended monitoring design criteria.

17. KEY WORDS AND DOCUMENT ANALYSIS

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FOREWORD

The Environmental Protection Agency was established to coordinate administration of the major Federal programs designed to protect the quality of our environment.

An important part of the Agency's effort involves the search for information about environmental problems, management techniques and new technologies through which optimum use of the Nation's air, land, and water resources can be assured and the threat pollution poses to the welfare of the American people can be minimized.

EPA's Office of Research and Development conducts this search through a nationwide network of research facilities. As one of these facilities, the Robert S. Kerr Environmental Research Laboratory is the Agency's center of expertise for investigation of the soil and subsurface environment. Personnel at the laboratory are responsible for management of research programs to: (a) determine the fate, transport and transformation rates of pollutants in the soil, the unsaturated zone and the saturated zones of the subsurface environment; (b) define the processes to be used in characterizing the soil and subsurface environment as a receptor of pollutants; (c) develop techniques for predicting the effect of pollutants on ground water, soil and indigenous organisms; and (d) define and demonstrate the applicability and limitations of using natural processes, indigenous to the soil and subsurface environment, for the protection of this resource.

This report contributes to that knowledge which is essential in order for EPA to establish and enforce pollution control standards which are reasonable, cost effective, and provide adequate environmental protection for the American public.

The subsurface environment of ground water presents many challenges to effective monitoring efforts. Physical, microbiological and geochemical forces interact over variable time frames as ground-water quality characteristics evolve. Monitoring data should be collected with minimum disturbance of the subsurface. This goal implies careful attention to the details of sound drilling, well construction, and sampling methodologies.

The complex nature of ground-water monitoring further demands that cost-effective choices of materials, target chemical constituents, and procedures are made prior to implementation of the network design. Attempts to cut costs for the sake of short-term "savings" can result in substantial added expense. This may occur when the goals of the monitoring effort are expanded and information needs require increased analytical detail. There are few merits to penny-wise, pound-foolish approaches to ground-water monitoring.

Clinton W. Hall

Clinton W. Hall
Director
Robert S. Kerr Environmental Research Laboratory

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SECTION 1
INTRODUCTION

Ground water provides the base flow of all perennial streams and over 90 percent of the world's freshwater resources. Ground water also is a source of one-half of the United States' drinking water supplies (1). Yet until recently ground water has received only token scientific attention in terms of its quality and protection. Insufficient attention has been given to proper monitoring procedures to accurately determine the quality of ground water.

With the beginning of the industrial age, a variety of new chemicals were introduced into the hydrologic cycle by man's indiscriminate use and waste disposal activities. "Since World War II, the explosive development of the synthetic chemical industry added thousands of additional chemicals to the environment. *Chemical Abstracts* announced in March 1972 that it had registered 2,000,000 unique chemicals since January 1965" (2). A large number of these organic and inorganic chemicals enter both surface water and ground water not only through waste disposal but also as a result of normal use of these water resources.

The presence of many trace substances in ground water, even at very low concentrations, may create short-term or long-term health hazards (3). The inclusion of approximately 113 organic chemicals on the EPA priority pollutant list indicates the significance accorded these chemicals by U.S. health officials.

The passage of the Safe Drinking Water Act (PL 93-523) in 1974 finally recognized ground water as a major source of drinking water and established standards of ground-water quality protection. Later, passage of the Toxic Substance Control Act (PL 94-469) and the Resource Conservation and Recovery Act (PL 94-480) further recognized the significance of ground water resources and the importance of their protection against the threats increasingly posed by human activities.

Regulatory agencies are charged with regulating the disposal of waste to insure that the environment is not adversely affected. To accomplish this task, these agencies must set design and operational standards based on available technology to minimize potential pollution. Disposal facilities then must comply with these standards and monitor the effects of their operation on the surrounding environment. The use of wells or piezometers for collecting water samples and water level data has been and probably will continue to be the method for monitoring the effects of waste disposal facilities on ground water.

Considerable research has been conducted to develop analytical laboratory techniques to detect the low levels of the many constituents named in water quality standards or legislation related to ground-water protection or waste management practice. Monitoring well construction, water sample collection, and preservation techniques have been established by several different laboratories and agencies in an attempt to insure that water samples delivered to the laboratory are chemically representative of the water contained in the ground. However, there is considerable controversy among laboratories, agency policies, and researchers concerning proper well construction and sampling techniques and appropriate procedures for preserving the original chemical character of the samples. If monitoring wells and water samples are to provide the performance yardstick for disposal facilities' design and operation, the significance of various monitoring well construction and sampling procedures and preservation techniques must be determined.

Need for and Importance of Monitoring

Ground-water monitoring is essential to determine the quality of the nation's ground-water resources and the effectiveness of ground-water pollution control regulations. Only through the collection of accurate data can we ascertain the chemical nature of our ground-water resources. Ground-water monitoring can be divided into four types: *ambient* monitoring, *source* monitoring, *case preparation* monitoring, and *research* monitoring.

Ambient ground-water quality monitoring establishes an understanding of characteristic regional water quality variations and changes over time. This type of monitoring is normally accomplished through routine sampling of wells on an areal or regional basis. The wells sampled are often public water supply, industrial or domestic wells as opposed to specially constructed monitoring wells. The sample collection techniques also are often quite different from those for monitoring wells. Therefore, data obtained from ambient monitoring programs may not be comparable to that obtained by more rigorous well construction and sampling procedures. However, the data are invaluable in detecting significant changes in water quality and protecting public health.

Source monitoring is the type normally conducted at a potential pollution source. *Source* monitoring detects and quantifies the migration of pollutants from potential pollution sources. Most regulatory programs have monitoring guidelines that detail minimum standards for source monitoring. In an effort to minimize cost to the regulated community, a two-step approach to source monitoring has been used by most states.

The first step is a minimum-requirement approach based on the principle of detecting leakage of pollutants from disposal or storage facilities. It is understood that data collected from a detective monitoring scheme will not define the extent or seriousness of a developing problem. Therefore, once the detective monitoring system has sounded the alarm, most states require a more definitive monitoring program to provide interpretive information concerning the extent and seriousness of the problem.

The second step is interpretive monitoring which normally requires expanded information needs and the installation of additional wells. The purpose of interpretive monitoring is to define the limits and concentrations within the plume of pollutants moving from the presumed source. The addition of wells areally, and vertically nested well sets often is required to adequately define plume geometry and concentration gradients.

Case-preparation or *enforcement* monitoring is undertaken by the regulatory community to collect evidence for prosecution of ground-water pollution cases. This type of monitoring usually is developed in response to the language in the appropriate laws intended to be used in the prosecution of the case. The detailed information resulting from this type of monitoring generally is more specific with respect to concentrations and changes in concentrations at the legal points of regulation. Further definition of plume geometry or concentrations normally is not required for successful litigation.

Research monitoring often results in a level of data collection far beyond that required for other types of monitoring activities. Added information is required to help understand and document the mechanisms controlling solute transport of pollutants. The collection of this type of monitoring data is very rigorous and demanding although limited to specific research goals.

Selection of the types and levels of monitoring to be used in any situation should be made with care and judgment. The goals of a proposed monitoring program should be clearly stated and understood before consideration is given to what types of wells should be constructed, where they should be located, how deep they should be, what materials should be used, what chemical constituents should be analyzed, and how samples should be collected. Successful and cost-effective monitoring at all levels can be accomplished only after the goals or purposes of the monitoring program are thoroughly understood.

SECTION 2
OBJECTIVES

This publication was produced as part of a cooperative agreement between the Illinois State Water Survey and the U.S. Environmental Protection Agency (EPA CR 809966-01). The objectives of this project are as follows:

1) To assess the state of our knowledge of the potential effects of well construction and pump and sampling materials on the integrity of ground-water samples, and

2) To develop a guide that will facilitate the selection of pumps and devices used to collect water samples, and materials used in the construction of monitoring wells.

To achieve these objectives, the project was divided into two phases. Phase One entailed a thorough investigation and assessment of the existing literature. Phase Two involved laboratory and field studies to identify and assess efficient sampling techniques and materials for ground-water monitoring near waste disposal sites.

This manual represents the culmination of the work in Phase One of the project. It aspires to fill in the gaps left by previous studies of ground-water monitoring. Subject areas unexplored or treated superficially in the past are examined here in detail to present a more complete exposition of ground-water monitoring. These areas include the effects of materials on water samples, and the cost of materials vs the cost of the total monitoring project. Cost is addressed from an important, but often overlooked, perspective: How the initial investment in materials suitable for a particular monitoring project can pay dividends in terms of lower overall project cost. Use of appropriate materials can obviate the need for the additional work involved in designing and constructing new wells and in repeating sampling and analysis efforts when the use of inappropriate materials renders monitoring results unrepresentative of *in-situ* ground-water quality.

SECTION 3
GROUNDWATER MONITORING REQUIREMENTS

Requirements for ground-water monitoring exist at both the federal and the state levels. At the federal level, the Resource Conservation and Recovery Act (RCRA) and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) provide for monitoring to regulate hazardous wastes from generation to disposal to cleanup of substances accidentally released into the ground-water environment.

The Resource Conservation and Recovery Act (RCRA)

Ground-water monitoring at applicable hazardous waste management facilities is required by regulations issued pursuant to RCRA (Subpart F of 40 CFR Parts 264 and 265). While there are many intricate provisions in these rules, it is important to stress here that there are three basic monitoring objectives, and that there are two sets of requirements, one for existing facilities prior to permitting (Part 265) and one for permitted facilities (Part 264). The basic monitoring objectives are 1) to detect whether or not a facility is discharging hazardous wastes to the uppermost aquifer; 2) to determine whether concentrations of specific hazardous waste constituents are within prescribed limits; and 3) to measure the effectiveness of corrective actions.

Prior to permitting, the rules are standardized. All facilities follow the same rules and the rules are self-implementing. That is, for existing (interim status) facilities the parameter selection is pre-set. This means that the federal rules provide no authority for the regulatory agency to require the use of specific materials or equipment for well construction or sampling. However, during the permitting process, the regulatory agency will have the authority to evaluate an applicant's proposals and to make final specifications concerning well construction and sampling in the facility permit. Therefore, a major function of this document will be to provide a resource document to assist applicants and permit writers in making these important determinations.

The RCRA monitoring regulations (Parts 264 and 265) also require facility owners or operators to develop sampling and analysis programs which include monitoring parameters, sampling schedules, sampling procedures, sample preservation and shipping procedures, and analytical procedures.

For disposal facilities, the RCRA monitoring requirements are applicable throughout the post-closure care period (Subpart G of 40 CFR Parts 264 and 265).

The Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA)

While RCRA created one of the largest regulatory programs enacted by the federal government to protect ground water, it could not address the problem of abandoned waste sites or accidental spills of hazardous substances. For this reason, Congress enacted CERCLA to deal with the cleanup problems created by those uncontrolled hazardous waste sites where reponsibility cannot be assigned (e.g., abandoned sites) and accidents in the handling or transportation of hazardous substances. The Act provides for the generation of a trust (called Superfund) to finance the emergency cleanup of accidentally released hazardous substances and to assume the financial liability of closed permitted sites.

At present, no specific systems of ground-water monitoring are required by CERCLA. If hazardous contaminants from a waste facility or accidental spill are suspected or known to be entering the ground water, the choice of monitoring equipment and methodology to be used to determine the scope of the contamination is left to the states. Monitoring systems may be patterned after those outlined in RCRA, or states may develop systems of their own. Like the post-closure monitoring requirements of RCRA, those of CERCLA are relatively vague and untested. As they are applied in more cases, more specific recommendations, and perhaps regulations, for ground-water monitoring may develop.

State Requirements for Ground-Water Monitoring

Individual states may have their own requirements for ground-water monitoring. While EPA allows states to take authority for imposing monitoring requirements under RCRA and CERCLA, the actual requirements mandated by the various states may be more stringent than those of these two acts. For this reason, it is important that those involved in ground-water monitoring be familiar with the requirements of the state in which the monitoring is being performed. Such information usually can be obtained from the state's Environmental Protection Agency.

SECTION 4
BACKGROUND

Previous Studies

This section presents an overview of work previously published on the subject of ground-water monitoring. These works cover various aspects of monitoring in general, well design and construction, well sampling, and materials' considerations for use in monitoring applications.

Monitoring in General

The need for groundwater monitoring is evidenced in an article by Pettyjohn et al. (4), which presents an overview of the prevalence and significance of organic contamination in ground water. He explains where these organic compounds originate and includes observations on their chemistry, toxicity, mobility, sorption, volatility, dilution, biodegradation, and abiotic degradation.

A number of authors and researchers address the federal and state regulations that mandate monitoring. The National Council of the Paper Industry for Air and Stream Improvement (NCASI) (5) has prepared a Guide to Groundwater Sampling that describes the regulations developed under the Resource Conservation and Recovery Act (RCRA). The Council highlights requirements for system design, sampling and analysis, and monitoring preparation, evaluation and response. A USEPA publication (6) provides guidance for owners and operators of hazardous-waste land disposal facilities in complying with the interim status requirements for ground-water quality monitoring in Subpart F of 40 CFR 265. Clark and Sabel (7) report on a survey conducted to learn of states' requirements for monitoring wells, chemical analyses, and data interpretation.

The importance of defining the purpose of the monitoring program before designing the monitoring system is addressed by Geraghty and Miller, Inc. (8). They note that site-specific hydrogeologic data also play a part in system design and describe elements of a comprehensive hydrogeologic investigation. On monitoring in general, they address the design and installation of monitoring well networks, including determining the number and location of wells; selecting well casing and screen materials; and backfilling, sealing, developing and completing monitoring wells. They also discuss sampling protocol.

Grisak et al. (9) identify the technical difficulties involved in monitoring ground-water quality. Past ground-water monitoring efforts are critiqued by Todd et al. (10). A manual prepared for the USEPA by Fenn et al. (11) presents a comprehensive discussion of the many aspects of ground-water monitoring. Written to address monitoring at solid waste disposal facilities in particular, the manual also covers general monitoring principles, including network design; monitoring and well technology;

ground-water contamination by leachates; sample withdrawal, preservation and storage; and analytical methods.

Fenn et al. (11) discuss the methodology of various monitoring techniques, including wells screened or opened over a single vertical section of aquifer, piezometers, well clusters, single wells with multiple sample points, sampling during drilling, and pore water extraction from core samples. They list the advantages and disadvantages of each of these techniques and advise how to implement them. Estimates of the costs involved for the alternatives are supplied.

Tinlin (12) shows, by example, site-specific procedures for monitoring various classes of ground-water pollution sources. He covers brine disposal, plating waste contamination, landfill leachate, oxidation ponds, and multiple-source nitrate pollution.

Monitoring Well Design and Construction

Lewis (13) stresses the importance of custom-designing ground-water monitoring systems for specific monitoring objectives which are compatible with local hydrogeologic and chemical conditions.

Dunlap et al. (14) describe technology for construction of wells capable of providing representative, uncontaminated samples of ground water. Scalf et al. (1) and Sisk (15) detail various techniques for constructing monitoring wells, highlighting advantages and disadvantages of each method listed. Well construction practices are elaborated upon in a manual developed for EPA by the National Water Well Association (16), which sets forth standards prepared by NWWA for engineers and government personnel whose expertise is not in the field of well construction.

Selection of an appropriate well casing and screen for monitoring well applications is addressed by Fenn et al. (11). Pettyjohn et al. (17) discuss well casings and sampling equipment made from glass, Teflon®, stainless steel, polypropylene, polyethylene, other plastics and metals, and rubber, and suggest which materials are best suited to sampling for organic contaminants. A manual that reviews the proper selection, installation and utilization of thermoplastic water well casing has been published by the National Water Well Association and the Plastic Pipe Institute (18).

Seanor and Brannaka (3) discuss the potential effects of well construction, including well construction materials and drilling, on the results of organic water quality analyses. The *Manual of Ground-Water Quality Sampling Procedures* by Scalf et al. (1) describes the principles of operation and the advantages and disadvantages of the more common types of drilling techniques suitable for construction of ground-water monitoring wells, as does Fenn et al. (11).

Considerations for the selection of a drilling method are outlined by Minning (19), who addresses common drilling and sampling procedures for hazardous waste facilities. He also compares various aspects of different drilling methods, including cost, effectiveness in various formations, depth capability, cross-contamination potential, and quality of samples. Luhdorff and Scalmanini (20) present a methodology for rating several drilling methods based on their ability to achieve typical tasks in a ground-water quality investigation. They illustrate the application of the rating system to two ground-water contamination problems in California.

Ground-Water Sampling

Recommended methods of acquiring water data are presented by the USGS in a handbook published by its Office of Water Data Coordination (21). Scalf et al. (1) cover ground-water sampling comprehensively in a manual published by the National Water Well Association. The manual presents considerations in the selection of sampling procedures, including objectives of the sampling program, characteristics and nature of pollutants, and hydrogeology of the area. It also describes procedures currently utilized to sample ground water and highlights advantages and disadvantages of each. Sisk (15) also discusses sample parameter selection and sampling considerations. He further describes various types of monitoring wells and presents examples that suggest appropriate sampling procedures for each.

Gibb et al. (22) provide recommendations on sampling protocol and sample preparation, preservation, and storage, noting how these sampling steps can affect the chemical composition of the water samples. Grant (23) also provides information on sample collection and preservation. He describes grab or discrete sampling and composite sampling and explains the differences between them. Wood (24) offers guidelines for collection and field analysis of ground-water samples for selected unstable constituents. Schmidt (25) addresses sample collection, too, and speaks to the question of optimum pumping rates and duration prior to sampling. Scalf et al. (1) go farther and discuss sample records and chain-of-custody procedures. Others that detail the basics of sample withdrawal, preservation and storage include Carriere and Canter (26) and Fenn et al. (11).

General guidelines for volume requirements, container preference, preservative measures, and holding times when sampling for specific parameters are provided in a useful table by Fenn et al. (11).

Suggestions as to types of sample containers and preservation techniques to use when analyzing for various parameters can be found in many of the monitoring publications mentioned throughout this section. Regulatory agencies also may stipulate specific recommended practices. Several sources that deal with the effects of using particular containers in the presence of certain contaminants include King et al. (27), Struempler (28), Laterall et al. (29), and Coyne and Collins (30).

Sampling of purgeable organic compounds performed as part of the National Organic Monitoring Survey conducted by the USEPA is described by Brass et al. (31). A study by Dunlap et al. (14) that presents methods for acquiring grab samples of ground water suitable for total organic analysis, as well as other sampling information, aims to provide a basic capability for sampling for organic pollutants in shallow subsurface environments. Goerlitz and Brown (32) recommend preservation techniques for organic substances in water.

The potential for contamination posed by equipment and instrumentation used in ground-water monitoring is described by Seanor and Brannaka (3). They discuss the use of bailers and various pumps and describe how such sampling equipment can alter the chemical properties of ground water.

Todd et al. (10) highlight the need to check out the effects of sampling materials on analytical results for the contaminants of interest. This type of research was performed by Gibb et al. (22), who studied four types of pumps to determine their effects on water samples.

Selection criteria for pumps are offered by Gass et al (33). A number of authors detail various pumping and water collection devices, including McMillion and Keeley (34), Buss and Bandt (35), and Tomson et al. (36).

Everett et al. (37) provide detailed cost data for various monitoring methods and techniques. They also supply a breakdown of capital and operational costs and suggest sources of information for updating the cost estimates provided. Fenn et al. (11) also offer cost estimates for various monitoring techniques and well construction methods. To aid in the selection of monitoring methods, Tinlin (12) presents hypothetical illustrative examples for making decisions based, in part, on cost comparisons among monitoring alternatives.

Materials Used In Monitoring Efforts

Scalf et al. (1) offer guidelines in the selection of well construction materials when sampling for specific contaminants in Appendix A of their manual. An EPA report prepared by Geraghty and Miller, Inc. (8) names materials best suited to monitoring efforts and notes exceptions to their general recommendations. Pettyjohn et al. (17) suggest materials of choice when sampling for organic contaminants.

A number of researchers and authors detail the limitations inherent in using certain well construction materials. Scalf et al. (1) cite the high cost of Teflon®-constructed wells, and a USGS study by Imbrigiotta and Martin (38) draws attention to PVC's drawbacks in terms of its lack of physical strength and its susceptibility to damage. The same study points out that metallic casing materials may be subject to chemical degradation or dissolution.

Some previous studies provide in-depth analyses of these and other problems relating to compatibility of well construction and sampling materials with various contaminants. Miller (39) reports results of a laboratory study that aimed to identify chemicals that may leach from well casing material when it is exposed to selected pollutants and to quantify adsorption of selected pollutants on various well-casing materials. The leaching of organic and organotin compounds from PVC and CPVC pipe was documented in a USEPA report by Boettner et al. (40).

Gass et al. (33) describes the various metals used in water well applications, particularly in well pumps, and the types of corrosion that may afflict them. He also lists well and pump construction materials in order of preference based on their resistance to certain types of corrosion. Seanor and Brannaka (3) point out the potential sample contamination posed by steel casing, which is exposed to oils and solvents in its production. Another report by Fenn et al. (11) highlights the advantages of PVC casing over metals, and the contamination of ground water by the adhesives and primers associated with synthetic well casings has been addressed by Sosebee et al. (41).

The Uni-Bell Plastic Pipe Association (42) issued a report that describes the results of research into the control of residual vinyl chloride monomer (RVCM) in PVC water pipe. Dressman and McFarren (43) and Sachs and Banzer (44) addressed this same topic, as did Mantell and others (45). Berens and Daniels (46) discussed the prediction of vinyl chloride monomer migration from rigid PVC pipe. Earlier, Daniels and Proctor (47) reported on the extraction of RVCM from PVC bottles.

Curran and Tomson (48) describe the leaching of low levels of contaminants from tubing made from various materials. Junk et al. (49) detail organic contamination contributed to water samples by certain tubing materials. Study results on the adsorption of specific contaminants on walls of containers made from certain materials are reported by Massee et al. (50), Shendrikar et al. (51), Robertson (52,53), and Eicholz et al. (54).

Current Research Efforts

Monitoring methodology research presently is being conducted through three principal EPA programs as well as through a number of U.S. Geological Survey projects, private consultants, and foreign organizations. The EPA programs addressing sampling methodology include the Ground Water Research Branch of the Robert S. Kerr Environmental Research Laboratory in Ada, Oklahoma; the Ground Water Branch of the Environmental Monitoring and Support Laboratory in Las Vegas, Nevada; and the Solid and Hazardous Waste Research Section of the Municipal and Environmental Research Laboratory in Cincinnati, Ohio.

Research at RSKERL-Ada is directed principally at defining the processes which control the movement of contaminants through the subsurface. Currently, two activities sponsored by RSKERL specifically address sampling ground water for monitoring purposes. Through a cooperative agreement with the National Center for Ground Water Research, the University of Oklahoma is investigating the possible sorption of specific trace organic pollutants and metals from ground water onto the surface of monitoring well casing materials and the possible leaching or release of such substances from well casing materials into sampled water. Another cooperative agreement with the Illinois State Water Survey, partially supported by EMSL-Las Vegas, seeks to evaluate and develop methods for constructing, completing, and sampling ground-water monitoring wells to obtain representative physical, chemical, and biological analyses. This manual is a product of that research effort.

Several projects in the RSKERL program have sampling components indirectly related to ground-water monitoring. These are concerned primarily with collecting ground water and uncontaminated subsurface material for various research projects. Cores of subsurface materials are being used to measure physical, chemical, and microbial characteristics and to relate these to the ability of the subsurface to attenuate pollutant movement.

Stanford University has an extensive research project designed to evaluate ground-water contamination risks resulting from hazardous waste disposal. A portion of this project involves extensive sampling of ground water at field installations by the University of Waterloo.

EMSL-Las Vegas is active in several research areas directly related to ground-water monitoring. In addition to co-sponsoring the Illinois effort with RSKERL-Ada, EMSL-Las Vegas supports research into both drilling and non-drilling techniques for ground-water monitoring as well as into methods for vadose zone monitoring at hazardous waste sites. Methods under investigation that require drilling include down-hole sensors for small diameter boreholes, indicator parameters for hazardous constituents, x-ray fluorescence and infrared spectrometry screening for hazardous wastes, and compound-specific ground-water monitoring using fiber optics technology in combination with laser fluorescence spectroscopy.

Considerable effort at EMSL-Las Vegas is directed toward monitoring ground-water quality using non-drilling or remote-sensing techniques, especially at hazardous waste sites. One project is investigating the feasibility of sampling by cone penetrometer in lieu of conventional drilled wells. Other projects involve using geophysical methods such as complex resistivity for tracking leachates from hazardous waste sites.

Research at MERL-Cincinnati does not specifically address ground-water monitoring. The emphasis there is on providing technical support to RCRA and Superfund activities of the Agency. Most research is related to remedial action activities at waste disposal sites and/or the evaluation of the effectiveness of these activities. Ground-water monitoring is necessarily a part of such evaluations, but development of new monitoring techniques is generally not a part of MERL's research efforts.

SECTION 5
MONITORING WELLS AND SAMPLING APPARATUS

The success of a ground-water monitoring program depends, in part, on the selection of the proper type of well.

Production or traditional wells often are used to obtain samples in ambient ground-water monitoring programs. Designed to yield large quantities of turbidity-free water for potable or irrigation supplies, these wells generally tap the more permeable portions of an aquifer. Chemical data obtained from these wells depict the quality of water being delivered to the user community. Because water pumped from these wells is a composite of water from different horizontal and vertical strata in the aquifer systems, the presence of relatively narrow or small plumes of polluted water can be masked by dilution with water obtained from unaffected portions of the aquifer.

Production or traditional wells should not be used for the more detailed source, case-preparation, and research types of monitoring. Such detailed monitoring efforts call for wells designed to determine the ground-water quality at a given location and depth within the geologic materials being monitored. All available geologic and hydrologic information for the site of interest should be reviewed prior to selecting preliminary locations and depths for monitoring wells. The potential paths of pollutant movement from the site should be estimated and wells should be placed so that they can effectively and quickly detect releases. Information gained during the drilling process should be used to modify the monitoring plan to make it more effective.

Monitoring Well Components

The principal reason for constructing monitoring wells is to collect ground-water samples which, upon analysis, enable describing a contaminant plume and tracking movement of specific chemical or biological constituents. Obviously, the location of monitoring wells spatially and vertically is important. Of equal importance is the design and construction of monitoring wells to provide easily obtainable samples that will yield reliable, meaningful information. In general, monitoring well design and construction follow production well design and construction techniques. However, emphasis is placed on the effect these practices may have on the chemistry of the water samples being collected rather than on maximizing well efficiency.

From this emphasis, it follows that an understanding of the chemistry of the suspected pollutants and the geologic setting in which the monitoring wells are constructed plays a major role in the drilling technique and materials used. There are several components to be considered in the design of a monitoring well, including location, diameter, depth, casing, screen, sealing material, and well development. As these components are discussed in detail, it may be helpful to refer to Figure 5-1, which portrays two typical well installations: one for water supply and the other for ground-water quality monitoring.

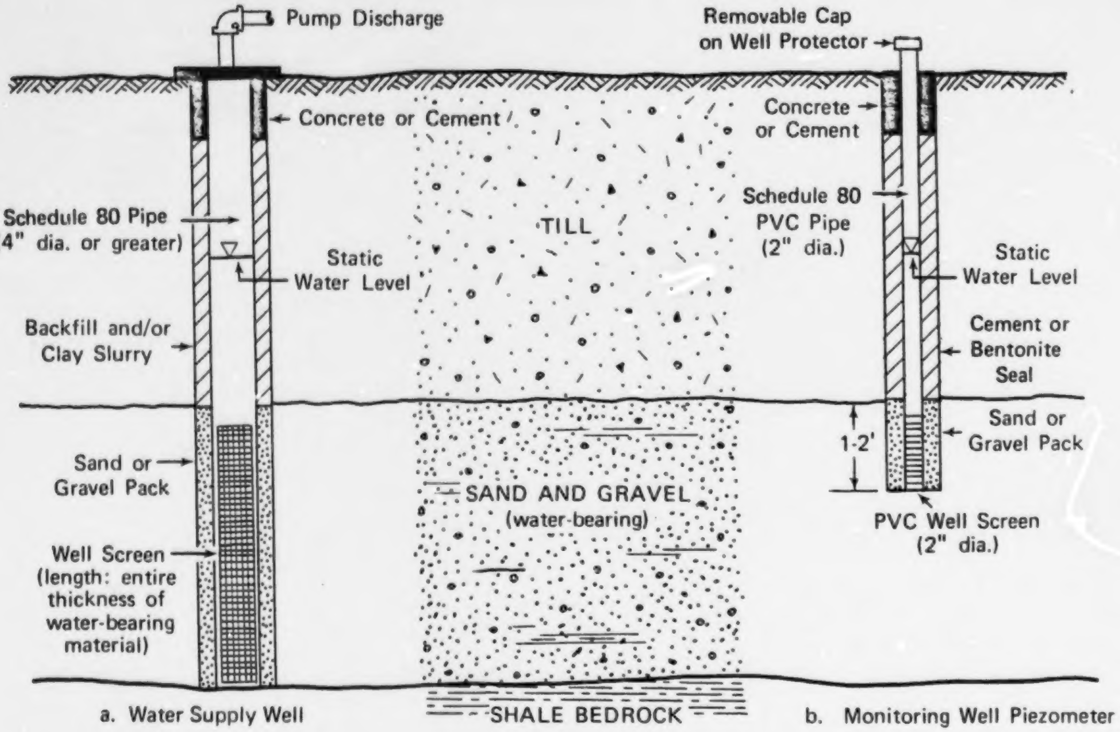

Pump Discharge
Concrete or Cement
Schedule 80 Pipe (4" dia. or greater)
Static Water Level
Backfill and/or Clay Slurry
Sand or Gravel Pack
Well Screen (length: entire thickness of water-bearing material)
a. Water Supply Well
TILL
SAND AND GRAVEL (water-bearing)
SHALE BEDROCK
Removable Cap on Well Protector
Concrete or Cement
Schedule 80 PVC Pipe (2" dia.)
Static Water Level
Cement or Bentonite Seal
Sand or Gravel Pack
1-2'
PVC Well Screen (2" dia.)
b. Monitoring Well Piezometer

Figure 5-1. Schematic diagrams of typical water supply (a) and monitoring (b) well installations

Well Location

The location of a monitoring well should be selected on the basis of the purpose of the program. This purpose may be to verify predictions of contaminant migration; to detect contaminants in drinking water supplies and thus protect public health; to activate a contingency plan such as a program for leachate collection; to protect the operator; or to reassure the public by demonstrating that their water quality is being monitored. Each of these purposes will require a somewhat specialized array of monitoring points and a somewhat different sampling program. The monitoring system must be designed to suit the purpose(s) in mind.

The positioning of a monitoring point in a contaminant flow path for an "interpretive" monitoring effort must be determined on the basis of reliable preliminary data. To do this, the contaminant flow path must be clearly defined in three dimensions during the "detective" phase. Only then can the optimum location for proposed monitoring wells be effectively determined.

Well Diameter

A domestic water supply well is commonly 4 inches in diameter to accommodate a submersible pump capable of delivering 5-10 gallons per minute. Municipal and industrial supply wells have greater diameters to handle larger pumps and to increase the available screened open area so the well can produce water more efficiently. Like that of a water supply well, the diameter of a monitoring well is determined by the size of the sampling device or pump. This strategy works well in very permeable formations, but unlike most water supply wells, monitoring wells are quite often completed in very marginal water-producing zones. Pumping one or more well volumes of water from a monitoring well built in such zones may present a serious problem if the well has a large diameter. Large quantities of water must be disposed of, and it may take several hours or even days for enough water to return to the well for successful collection of a representative sample. With the advent of several commercially available small-diameter pumps (less than 2 inches outside diameter) capable of lifting water from several hundred feet, it is rarely necessary to construct monitoring wells larger than 2 inches in diameter. Additionally, the smaller the diameter, the less it will cost for drilling and construction. A thorough discussion of advantages and disadvantages of monitoring well diameter has recently been published (55).

Well Depth

The depth of each monitoring well normally is determined by the geohydrologic conditions at the site being monitored. Most "detective" monitoring wells are completed in the first relatively permeable water-bearing zone encountered, since potential pollution sources requiring the installation of monitoring wells are frequently at ground surface. Locating the monitoring well in the first relatively permeable zone therefore yields an early warning of the migration of pollutants in most situations. However, care must be taken to assure the well is completed at a depth sufficient to allow for seasonal water table fluctuations. Under confined or semi-confined (leaky) conditions the water level will rise above the top of the water-bearing zone. In this instance, the well should be finished in the water-bearing zone and not above it.

If the water-bearing zone is thick (greater than 10 feet) or contamination is known or suspected in deeper formations, multiple wells completed at different depths should be used. For sampling at various depths, some engineers have nested several wells in a single borehole. This requires drilling a large diameter hole and exercising special care to ensure that the vertical integrity of the sampling points is maintained. It is important that monitoring wells be constructed so that they are depth-discrete, that is, so that they sample from one specific formation or zone without interconnection to others. To assure that this requirement is met, provisions for placing cement grout above and, if necessary, below the intake portion of the well, must be made in the design of the well.

Well Design and Construction Materials

The type of material used for monitoring well casing can have a distinct effect on the quality of the water samples collected. Galvanized casing will impart iron, manganese, zinc and cadmium to many waters. Steel casing may impart iron and manganese to the water samples. PVC pipe has been shown to release and adsorb trace amounts of various organic constituents to water after prolonged exposure. PVC solvent cements used to attach sections of PVC pipe also have been shown to release significant quantities of organic compounds. Teflon® and glass are among the most inert materials that have been considered for monitoring well construction. Glass, however, is very difficult and expensive to use under most field conditions. Stainless steel also has been found to work satisfactorily. A detailed discussion of materials is presented in later portions of the text.

In many situations, it may be possible to compromise accuracy or precision for initial cost. For example, if the contaminants of interest are already defined and they do not include substances which might bleed from, sorb or interfere with other analytical methods, it might be reasonable to use wells cased with a less expensive material. Wells constructed of less-than-optimum materials might be used for sampling if identically constructed wells are available in both uncontaminated and contaminated parts of the aquifer to provide ground-water samples for use as "blanks." Obviously, such "blanks" may not address adequately problems of adsorption on or leaching from the casing material induced by contaminants in the ground water. Careful consideration is required in each individual case, and the analytical laboratory should be fully aware of construction materials used.

Care must be given to the preparation of the casing and well screen materials prior to installation. As a minimum, both should be washed with detergent and rinsed thoroughly with clean water. Care also should be taken to ensure that these and other sampling materials are protected from contamination by using some type of ground cover such as plastic sheeting for temporary storage in the work area.

All wells should allow free entry of water. They also should produce clear, silt-free water. For drinking water supplies, the reason is obvious: sediment in the raw water can create additional pumping and treatment costs and lead to the general unsuitability of the finished water. With monitoring wells, sediment-laden water can greatly lengthen filtering times and create chemical interferences with the collected samples.

Commercially manufactured well screens generally work best provided the proper slot size is chosen. In formations where fine sand, silt, and clay predominate, sawed or torch cut slots will not retain the material, and the well may clog. It may be helpful to have well screens of several slot-sizes on site so that the correct manufactured screen can be placed in the hole after the water-bearing materials have been inspected. Gravel-packing materials compatible with the selected screen size will further help retain fine materials and also allow freer entry of water into the well by creating a zone of higher permeability around the well.

Well screen length is an important consideration. When monitoring a potable-water-supply aquifer, the entire thickness of the water-bearing formation should be screened. This provides an integrated water sample similar to what would be found in the drinking water supply. A monitoring program to describe contaminant plume geometry requires sampling discrete intervals of the water-bearing formation. In this situation, screen lengths of no more than 5 feet (1.5 m) should be used. Thick aquifers would require completion of several wells at different depth intervals. In some situations, only the first water-bearing zone encountered will require monitoring. Here the "aquifer" may be only 6 inches to a few feet (0.2-2 m) thick, and the screen length should be limited to 1 or 2 feet (<1 m). Monitoring for low density organic solvents or hydrocarbons which may float on the water surface creates a special problem. In such a case, the screen must be long enough to extend above the water level in the formations so these lighter substances can enter the well.

It is critical that the screened portion of each monitoring well access ground water from a specific depth interval. Vertical movement of water in the vicinity of the intake and around the casing must be prevented to obtain samples representative of that in the formation of interest. Specifically, rainwater can infiltrate backfill materials and dilute or contaminate samples collected from the screened portion of the well. Vertical seepage of leachate or contaminated water from adjacent formations along the well casing also may produce unrepresentative samples for the depth interval being sampled. More serious indeed is the creation of a conduit in the annulus of a monitoring well which could contribute to or hasten the spread of contamination.

Monitoring wells usually are sealed with neat cement grout, dried bentonite, or bentonite slurry. While a neat cement grout often is recommended, shrinkage and cracking of the cement upon curing can create an improper seal. The use of bentonite traditionally has been considered more effective than neat cement grout. However, recent studies have shown that some organic compounds migrate through bentonite layers with little or no attenuation (56). Therefore, expanding cement appears to offer the greatest potential for the effective sealing of wells. There are several commercial formulations of this type of cement which generally is more chemical resistant than clays. The seal should extend from just above the well intake to a level above the highest known seasonal water level. Backfill cuttings then may be used to fill the annulus in the unsaturated zone provided that they are free of contamination, and a mounded, expanded cement collar can be placed around the well casing to divert surface drainage from the immediate area of the well casing. This collar should extend well below the frostline and should be checked periodically for cracks or fissures.

When sealing materials must be placed below the water table (or where water has risen in the borehole), it is recommended that they be pumped down the annulus through a tremie pipe and filled from the bottom upward.

Drilling Methods

The selection of a drilling method best suited for a particular installation is based on the following factors, listed in order of importance:

1) Hydrologic information
    a. types of formations
    b. depth of drilling
    c. depth of desired screen setting below water table
2) Types of pollutants expected
3) Location of drilling site, e.g., dry lands or inside a lagoon
4) Design of monitoring well desired
5) Availability of drilling equipment

The principles of operation and the advantages and disadvantages of the more common types of drilling techniques suitable for constructing ground-water monitoring wells are discussed by Scalf (1). The following is a brief summary of material presented in that publication.

Auger drilling frequently is accomplished by rotating a solid-stem, continuous-flight auger into the soil. As the augers are "screwed" into the soil, the cuttings are brought to the surface on the rotating flights. Auger bits are essentially of two types: fish tail or drag bits for use in unconsolidated materials, or claw or finger bits for use in consolidated or cemented soils. Once the desired depth is reached, the augers are allowed to rotate to clean out the borehole. The augers then are removed from the borehole and the well screen and casing installed. This method is best applied when installing monitoring wells in shallow unconsolidated formations that will maintain an open borehole long enough to permit emplacement of the well, piezometer, or sampling device.

Hollow-stem, continuous-flight auger drilling differs from the solid-stem augers in that the stem is hollow. Upon reaching the desired depth, a small-diameter casing and screen can be set inside the hollow stem. The augers then are pulled out as the casing is held in place. If the borehole stands open after withdrawing the augers, an artificial gravel pack is placed opposite the screened portion of the well. If the material collapses around the screened portion of the well, those materials are ultimately removed or altered in grain size by the development procedures employed after well construction.

Auger drilling rigs generally are mobile, fast, and inexpensive to operate in unconsolidated formations. Because no drilling fluid is required, contamination problems are minimized. However, these types of rigs cannot be used in hard-rock drilling. Depth limitations vary with the equipment and types of soils, but usually are a maximum of 150 feet. Collection of formation samples is not expedited by the use of solid-stem, continuous-flight augers. However, conventional soil sampling techniques (split spoon and Shelby tube sampling) can be accomplished effectively during the drilling procedure through the hollow-stem, continuous-flight augers. Formation sampling has been covered in detail by Scalf et al. (1).

Straight rotary drilling is accomplished by pumping a drilling mud down the inside of a rotating drill pipe and allowing it to return to the surface through the annulus. The drilling mud cools the drill bit, carries the cuttings to the surface, prevents excess fluid loss into the formation and prevents the formation from caving. The rotating drill pipe turns the bit, which cuts the formation, allowing the cuttings to be flushed out. The drilling fluid (or mud) may be clear water, water mixed with bentonite, or water mixed with various synthetic or natural drilling aids. Rotary rigs generally are available throughout the United States. They are capable of drilling in all types of formations to almost any depth desired for monitoring and are fairly reliable in most formations. Casing is not required during the drilling and logging of formations.

The use of drilling fluids or muds during construction can bias the results of samples collected from wells. The introduction of clear water has a tendency to allow water to migrate into permeable formations which may be of interest. This water must be effectively removed before the quality of "native ground water" can be determined. Drilling muds also present a problem during the well development and have the ability to affect the transport of certain pollutants as water moves toward the well. Organic-based muds add significant quantities of foreign organic material into the aquifer system (57,58,59). Studies concerning the effects of these types of muds on the analytical results of collected samples and the biodegradability of the muds have not been conclusive.

Air rotary rigs operate in the same manner as the mud rotary rig except that air is circulated down the drill pipe and returns with the cuttings up the annulus. Some rotary rigs are equipped to operate with either mud or air. Air rotary rigs are available throughout much of the United States and are well suited for many drilling applicatons.

Air rotary rigs operate best in hard rock formations. Formation water is blown out of the hole along with the cuttings, so it is possible to determine when the first water-bearing zone is encountered. After filtering of water blown from the hole, collection and field analyses may provide preliminary information regarding changes in water quality for some parameters. Formation sampling ranges from excellent in hard, dry formations to nonexistent when circulation is lost in cavernous limestones and other formations with cavities.

Casing is required to keep the borehole open when drilling in soft, caving formations below the water table. When more than one water-bearing zone is encountered and where the hydrostatic pressures are different, flow between zones will occur between the time when the drilling is done and the time when the hole can be properly cased and one zone grouted off. Commonly, no synthetic drilling aids are used in air rotary drilling. If the air is filtered to capture compressor lubricants, contamination can be minimized relative to other methods. The use of air rotary drilling in badly contaminated subsurface situations must be approached carefully to minimize the exposure of drilling personnel to potentially hazardous materials.

A cable tool rig uses a heavy, solid-steel chisel-type drill bit suspended on a steel cable which, when raised and dropped, chisels or pounds a hole through the soils and rock. When drilling through the unsaturated zone, some water must be added to the hole. Cuttings are suspended in the water and periodically bailed. After enough water enters the borehole to replace the water removed by bailing, no additional water needs to be added. When soft, caving formations are encountered, it is necessary to drive casing as the hole is advanced to prevent collapse of the hole. Often the drilling can be advanced only a few feet below the bottom of the casing. Because the drill bit is lowered through the casing, the hole created by the bit is smaller than the casing. Therefore, the casing (with a sharp, hardened casing shoe on the bottom) must be driven into the hole. The shoe, in fact, cuts a slightly larger hole than does the drill bit. This tight-fitting drive shoe cannot be relied upon to form a seal when overlying water-bearing zones are encountered.

Formation samples can be excellent when a skilled driller uses a sand-pump bailer. Information regarding water-bearing zones is readily available during drilling. Relative permeabilities and some water-quality data also can be obtained from different zones penetrated if a skilled operator is available. Cable tool rigs can operate satisfactorily in all formations, but they are best suited for large, caving, gravel-type formations or formations with large cavities above the water table.

Cable tool drilling is slow compared with rotary drilling. The necessity of driving the casing along with drilling in unconsolidated formations requires that the casing be pulled back to expose selected water-bearing zones. This process complicates the well completion process and often increases cost. Relatively large diameter casing is required (minimum 4-inch casing) which increases the costs compared with rotary drilled wells with plastic casing. The use of cable tool rigs for small-diameter (2-inch) wells is not recommended.

Reverse circulation drilling is accomplished by allowing water or mud to circulate down the annulus and up the inside of the drill pipe (reverse flow direction from direct rotary mud drilling). This type of drilling is used for construction of high-capacity production wells and is not suited for small, water-quality sampling wells. Custom drilling techniques may be necessary for specialized investigations (60).

Well Development

Development is a facet of monitoring-well construction that is often overlooked. During the drilling process, fines are forced into the open borehole, forming a mud cake that reduces the hydraulic conductivity of the materials opposite the screened portion of the well. To allow free entry of water into the monitoring well and to maximize well yields (a particularly important factor for low-yield geologic materials), this mud cake must be broken down and the fines removed from the well.

Additionally, monitoring wells must be developed to provide water free of suspended solids for sampling. When sampling for metal ions and other inorganic constituents, water samples must be filtered and preserved at the well site at the time of sample collection. Improperly developed monitoring wells will produce samples containing suspended sediments that will both bias the chemical analysis of the collected samples and frequently cause clogging of the field filtering mechanisms (61).

The development procedures used for monitoring wells are similar to those used for production wells. The basic principles include creating alternately high and low velocities of water flow in the well to break down the mud pack or loosen fines, followed by pumping to remove the fines from the well and the immediate area outside the well screen.

Successful development methods for relatively productive wells include the use of a surge block, bailing, and surging by pumping. A surge block is a plunger device that fits loosely inside the well casing. It is moved forcibly up and down, causing water to surge in and out of the well screen. After surging, the well must be pumped to remove the fines carried into the well screen and casing. The use of surge blocks for monitoring well development has not been widely attempted. The potential for damaging a relatively fragile, 2-inch-diameter PVC well with a tight-fitting surge block has generally overruled the potential benefits that would be gained from this type of development.

A bailer sufficiently heavy to fall quickly through the water can be raised and lowered rapidly through the screened portion of the well. This action will create the same alternating surging action as the surge block. The use of bailers for developing wells is more common than the use of the surge block.

Another method for developing wells in relatively productive geologic materials is to surge either with a pump or by air. When using a pump, the well is alternately pumped and left idle to simulate the surging action desired to loosen the fines and remove them from the well. However, in most applications, no outward movement of water from the well is experienced, and bridging of fines moving toward the well limits the effectiveness of this technique.

When pumping with air, the effectiveness of the procedure depends on the geometry of the device injecting air into the well. Figure 5-2 illustrates a simple device

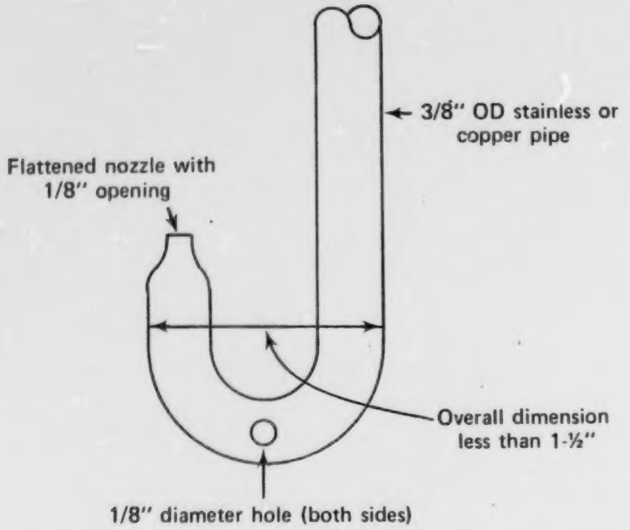

3/8" OD stainless or copper pipe
Flattened nozzle with 1/8" opening
Overall dimension less than 1-½"
1/8" diameter hole (both sides)

Figure 5-2. Schematic diagram of an air driven well development device

that diverts air through the well screen to loosen the fines and forces air, water and fines up the well casing and out of the well. These devices are particularly effective for developing monitoring wells in relatively productive geologic materials. Air development techniques also may cause the exposure of drilling personnel to hazardous materials when badly contaminated ground water is present. Careful precautions must be taken to minimize personnel exposure.

Development procedures for monitoring wells in relatively unproductive geologic materials is somewhat limited. Due to the low hydraulic conductivity of the materials, surging of water in and out of the well casing is extremely difficult. Also, when the well is pumped, the entry rate of water is inadequate to effectively remove fines from the well bore and the gravel pack material outside the well screen.

In this type of geologic setting, clean water can be circulated down the well casing, out through the screen and gravel pack, and up the open borehole prior to placement of the sealant in the annulus. Relatively high water velocities can be maintained and the mud cake from the borehole wall can be broken down effectively and removed. (Because of the low hydraulic conductivity of geologic materials outside the well, a negligible amount of water will penetrate the formation being monitored.) Immediately following this procedure, the well sealant should be installed and the well pumped.

In summary, all monitoring wells should be developed. The additional time and money spent for this important procedure will expedite sample filtration and result in samples more representative of water contained in the formation being monitored. The time saved in filtration alone will more than offset the cost of development.

Sampling Apparatus

Many brands of pumps are available for use in small-diameter (2-inch) wells. Table 5-1 lists selected commercially available sampling devices and their principal features. Devices in Table 5-1 can be divided into five general categories based on their methods of operation: bailers, suction lift pumps, gas contact samplers, positive displacement samplers, and syringe samplers.

Bailing is one of the simplest and oldest methods for sampling small-diameter monitoring wells. Bailers, which can be constructed from a wide variety of materials, require no power sources and are easy to transport. They are economical and easy to clean. One of the drawbacks of using a bailer is that it is time-consuming and sometimes impractical when dealing with large quantities of water. Special care also must be taken to keep the rope, wire, or chain clean during bailing to prevent the introduction of contaminants. The transfer of water from the bailer to the sample container may allow aeration of the sample and outgassing of volatile chemical constituents. Bottom-draw bailer designs with dual check valves minimize these sources of bias.

Suction lift sampling devices listed in Table 5-1 include peristaltic and Venturi-type pumps. The peristaltic pumps are relatively portable and can operate over a wide range of pumping rates. However, their use is limited to situations where water levels are less than about 20 feet. The suction created by the peristaltic pumping action changes pressure in the transfer lines and may result in degassing and loss of volatile organic compounds from the sample.

The Venturi pump operates in the same way as the domestic-size two-pipe jet pump. Water is pumped at the surface by a centrifugal pump. A portion of the water is circulated down a return pipe and through a Venturi section where suction is created, and water from the well is pulled into the Venturi section and up the discharge pipe. The pressure drop created at the Venturi section may cause degassing or volatilization of organic compounds. The circulation of water back into the Venturi section and priming vessel also makes it difficult to determine when a particular well volume is being delivered to the surface.

Gas-drive contact pumps normally use nitrogen gas to force water from a sampling chamber up through a discharge line. The surface-area-to-water ratio is small to minimize the effects of the gas contact. Data have not yet been obtained to accurately determine the effect of gas/water contact.

Positive displacement pumps listed in Table 5-1 include the helical-rotor, piston, and bladder-type pumps. All three can operate over a wide range of pumping rates. Though the pumps are relatively portable and easy to operate, they do require power (electricity or compressed gas) and are somewhat difficult to clean. Available data suggest that these pumps are more versatile and desirable than other devices for sampling most chemical constituents.

Syringe-type samplers are used to collect samples for analysis of volatile organic compounds. After purging the well with another pump, sampling devices are lowered into the well and positive pressure is maintained to prohibit the entry of water until the desired depth is reached. Pressure is then released, and the hydrostatic pressure in the well fills the syringe. The sample is raised to the surface and preserved for analysis.

Table 5-1. Saturated-Zone Sampling Devices for Use in Small-Diameter Boreholes and Monitoring Wells

Manufacturer	*Model name/ number*	*Principle of operation*	*Maximum outside diameter/length (inches)*	*Construction materials (w/lines & tubing)*	*Lift range (ft)*	*Delivery rates or volumes*	*1982 price (dollars)*	*Comments*
BarCad Systems, Inc.	BarCad Sampler	dedicated; gas drive (positive displacement)	1.5/16	PE, brass, nylon, aluminum oxide	0-150 with std. tubing	1 liter for each 10-15 ft of submergence	220-350	requires compressed gas; custom sizes and materials available; acts as piezometer
Cole-Parmer Inst. Co.	Master Flex 7570 Portable Sampling Pump	portable; peristaltic (suction)	<1.0/NA	(not submersible) Tygon®, silicone Viton®	0-30	670 mL/min with 7015-20 pump head	500-600	AC/DC; variable speed control available; other models may have different flow rates
ECO Pump Corp.	SAMPLifier	portable; venturi	<1.5 or <2.0/NA	PP, PE, PVC, SS, Teflon®, Tefzel®	0-100	0-500 mL/min depending on lift	400-700	AC, DC, or gasoline driven motors available; must be primed
Galtek Corp.	Bailer 219-4	portable; grab (positive displacement)	1.66/38	Teflon®	no limit	1075 mL	120-135	other sizes available
GeoEngineering, Inc.	GEO-MONITOR	dedicated; gas drive (positive displacement)	1.5/16	PE, PP, PVC, Viton®	probably 0-150	app. 1 liter for each 10 ft of submergence	185	acts as piezometer; requires compressed gas
Industrial and Environmental Analysts, Inc. (IEA)	Aquarius	portable; bladder (positive displacement)	1.75/43	SS, Teflon®, Viton®	0-250	0-2800 mL/min	1500-3000	requires compressed gas; other models available; AC, DC, manual operation possible
IEA	Syringe Sampler	portable; grab (positive displacement)	1.75/43	SS, Teflon®	no limit	850 mL sample vol.	1100	requires vacuum and/or pressure from hand pump
Instrument Specialties Co. (ISCO)	Model 2600 Well Sampler	portable; bladder (positive displacement)	1.75/50	PC, silicone, Teflon®, PP, PE, Delrin® acetal	0-150	0-7500 mL/min	990	requires compressed gas (40 psi minimum)
Keck Geophysical Instruments, Inc.	SP-81 Submersible Sampling Pump	portable; helical rotor (positive displacement)	1.75/25	SS, Teflon®, PP, EPDM, Viton®	0-160	0-4500 mL/min	3500	DC operated
Leonard Mold and Die Works, Inc.	GeoFilter Small Dia. Well Pump (#0500)	portable; bladder (positive displacement)	1.75/38	SS, Teflon®, PC, Neoprene®	0-400	0-3500 mL/min	1400-1500	requires compressed gas (55 PSI minimum); pneumatic or AC/DC control module
Oil Recovery Systems, Inc.	Surface Sampler	portable; grab (positive displacement)	1.75/12	acrylic, Delrin®	no limit	app. 250 mL	125-160	other materials and models available; for measuring thickness of "floating" contaminants
Q.E.D. Environmental Systems, Inc.	Well Wizard® Monitoring System (P-100)	dedicated; bladder (positive displacement)	1.66/36	PVC	0-230	0-2000 mL/min	300-400	requires compressed gas; piezometric level indicator; other materials available

Concluded on next page

Table 5-1. (Concluded)

Manufacturer	*Model name/ number*	*Principle of operation*	*Maximum outside diameter/length (inches)*	*Construction materials (w/lines & tubing)*	*Lift range (ft)*	*Delivery rates or volumes*	*1982 price (dollars)*	*Comments*
Randolph Austin Co.	Model 500 Vari-Flow Pump	portable; peristaltic (suction)	<0.5/N/A	(not submersible) rubber, Tygon®, or Neoprene®	0-30	see comments	1200-1300	flow rate dependent on motor and tubing selected, AC operated; other models available
Robert Bennett Co.	Model 180	portable; piston (positive displacement)	1.8/22	SS, Teflon®, Delrin®, PP, Viton® acrylic, PE	0-500	0-1800 mL/min	2600-2700	requires compressed gas; water level indicator and flow meter; custom models available
Slope Indicator Co. (SINCO)	Model 514124 Pneumatic Water Sampler	portable; gas drive (positive displacement)	1.9/18	PVC, nylon	0-1100	250 mL/flushing cycle	250-350	requires compressed gas; SS available; piezometer model available; dedicated model available
Solinst Canada Ltd.	5W Water Sampler	portable; grab (positive displacement)	1.9/27	PVC, brass, nylon, Neoprene®	0-330	500 mL	1300-1800	requires compressed gas; custom models available
TIMCO Mfg. Co., Inc.	Std. Bailer	portable; grab (positive displacement)	1.66/ custom	PVC, PP	no limit	250 mL/ft of bailer	20-60	other sizes, materials, models available; optional bottom-emptying device available; no solvents used
TIMCO	Air or Gas Lift Sampler	portable; gas drive (positive displacement)	1.66/30	PVC, Tygon®, Teflon®	0-150	350 mL/flushing cycle	100-200	requires compressed gas; other sizes, materials, models available; no solvents used
Tole Devices Co.	Sampling Pump	portable; bladder (positive displacement)	1.38/48	SS, silicone, Delrin®, Tygon®	0-125	0-4000 mL/min	800-1000	compressed gas required; DC control module; custom built

Construction Materials Abbreviations

PE	Polyethylene
PP	Polypropylene
PVC	Polyvinyl Chloride
SS	Stainless Steel
PC	Polycarbonate
EPDM	Ethylene-Propylene Diene (synthetic rubber)

Other Abbreviations

NA	Not Applicable
AC	Alternating Current
DC	Direct Current

NOTE: Other manufacturers market pumping devices which could be used for ground-water sampling, though not expressly designed for this purpose. The list is not meant to be all-inclusive and listing does not constitute endorsement for use. Information in the table is from sales literature and/or personal communication. No skimmer, scavenger-type, or high-capacity pumps are included.

In addition to the effects the pumping mechanism may have on the sample, the materials that contact water in the pump and delivery tubes also should be examined. Chemical constituents can be sorbed (adsorbed or absorbed)and leached from improperly selected materials in pumps. Considerations for materials selection is discussed later in Section 7 of this report.

Dedicated *in-situ* sampling devices also are available for saturated-zone sampling. These devices are placed directly into the geologic materials to be sampled and are pumped by gas-drive contact. The literature does not address the suitability of these devices for organic sampling.

In-line detection and sampling devices are valuable tools for ground-water monitoring. During the collection of samples, flow-through cells for monitoring temperature, pH, redox potential, and conductivity should be used. These devices should be constructed to allow for a constant flow of water without the accumulation of gases. The accumulation of gases on the probes can cause erroneous values to be recorded. Probes should be noncontaminating or as inert as possible.

As with well construction and drilling method precautions, all sampling devices should be carefully cleaned prior to use. A dilute hydrochloric acid rinse followed by successive rinses with deionized water, acetone, and distilled water are routinely recommended. In badly contaminated situations a hot water detergent wash prior to the above rinsing procedure may be necessary. Hexane rinses prior to the final distilled water rinse aid the removal of sparingly soluble organic materials prior to sampling for low-level organic pollutants.

SECTION 6
SAMPLING STRATEGY

The importance of proper sampling of monitoring wells cannot be overemphasized. Even when the wells are correctly located, constructed and developed, special precautions must be taken to ensure that the sample collected is representative of the ground water at that location. Care also is needed to ensure that the sample is neither altered nor contaminated by the sampling and handling procedures.

To select proper sampling procedures for monitoring wells, several basic questions must be reviewed. First, the purpose of the monitoring program and collection of samples must be reevaluated. Monitoring commonly is undertaken to comply with state or federal regulations that set forth a list of chemical constituents to be monitored. They also usually stipulate the concentrations of various chemical constituents that must be analyzed and reported. Sampling procedures for defining plume geometry and migration may require different procedures than those for routine regulatory monitoring. Sampling procedures for research projects may be particularly specialized and more demanding. In all instances, it is essential to develop a complete list of chemical parameters to be measured and the sensitivity at which they will be measured. Secondly, the physical limitations of the well and the well site must be considered. The diameter of the well, depth to water, length and location of the well screen, and accessibility of the well site all bear on the practical application of various sampling procedures.

Prior to discussing the effects of well flushing and pumping mechanisms on ground-water quality, it would be instructive to review briefly the factors controlling ground-water quality. An understanding of these factors enables one to better plan sampling efforts and minimize the effects of reactions that may occur due to sample handling.

Effects of Subsurface Conditions on Ground-Water Quality and Sampling

The subsurface is a condensed, geologic, and geochemical environment which also serves as a habitat for microorganisms (62,63). It is difficult to describe the entire range of subsurface conditions since local effects can drastically alter regional properties of temperature, pressure, oxidation-reduction potential, mineral solubility, solution chemistry, and biological activity. The relevance of average conditions must be evaluated on a case-by-case basis in order to account for the changes in ground-water chemistry which may occur during sample collection and retrieval. Temperature and pressure are major physical influences in this regard.

Temperature fluctuations in the upper 10 m (33 ft) of the subsurface occur in response to seasonal air temperature variations. In the United States, average ground-water temperatures range from 3°C to 25°C (37°F to 77°F) to a depth of 20 m (66 ft) (64). Local effects can be quite marked, however, since increases from 7°C to 16°C

(42°F to 60°F) above background have been observed in contaminated aquifers near landfills (65). Pressure gradients in the subsurface may be approximated as those due to the hydrostatic pressure of a column of water equivalent to the depth of interest. The strength of the pressure gradient may vary, though it is generally about 0.1 atm $\cdot$ m^{-1} (0.4-0.5 psi $\cdot$ ft^{-1}). Summarizing average physical conditions in the subsurface, one can expect that from the screened portion of a shallow monitoring well 10-20 m (33-66 ft) deep to the surface, temperature and pressure differentials may range from 10-30°C (45-83°F) and from 2-3 atm, respectively. Regardless of the choice of well construction methods or materials which contact the sample, the impact of temporal and spatial physical changes must be minimized to provide the most representative ground-water sample possible.

Chemical and biological indicators of subsurface conditions vary greatly in response to small changes in the above-mentioned physical factors. Considerations of sample handling procedures and the compatibility of materials with the ground-water system are subtle. In general, the subsurface environment is not in equilibrium with ambient surface conditions. This is particularly true of the atmospheric gases oxygen and carbon dioxide, which exert control over the oxidation-reduction potential, pH, buffer capacity, and chemical speciation of dissolved substances. Several reference works on aquatic and ground-water chemistry provide background information on the range of potential conditions to which samples, well casing, and sampling devices may be subjected (66,67,68,69).

Within an aquifer, there are six major processes which affect subsurface geochemistry. These are: 1) complex formation; 2) acid-base reactions; 3) oxidation-reduction processes; 4) precipitation-dissolution reactions; 5) sorptive interactions; and 6) microbiological processes.

All of these processes can be affected by sample collection procedures. Shifts in solution chemistry caused by rapid changes in temperature, pressure, or gas content may result in nonrepresentative samples. This is particularly true of the carbonate buffer system since ground water is normally oversaturated with carbon dioxide (CO_2). The system is sensitive to temperature and pressure changes since gaseous, dissolved, and solid chemical constituents participate in equilibrium reactions. For example, the loss of dissolved CO_2 on simultaneous temperature increase and sample depressurization will cause an increase in the pH. The pH changes in turn affect mineral solubility, the kinetics of iron and manganese oxidation, and hydrolysis reactions. Products of these reactions in turn may shift the chemical speciation of nutrients and metals and either stimulate or inhibit microbial activity.

Many potential changes can take place in a ground-water sample while being collected or before it is preserved (22,70). The previous discussion described general subsurface conditions and examples of solution chemical changes in inorganic constituents if samples are improperly collected. The impacts on volatile organic compound concentrations also can be quite marked. Samples collected from sites exhibiting unusual chemical properties may respond differently.

Effects of Hydrologic Conditions on Sampling Strategy

Hydrologic factors can exert controlling effects on the collection of representative samples. The yield potential of a monitoring well will determine the length of time that a well must be pumped at a given rate to produce a sample representative of the aquifer at that location. The transmissivity of the materials tapped by the well also is important in determining reasonable sampling frequencies and predicting rates of ground-water movement. To determine these parameters, well or slug tests should be conducted on the monitoring wells to be sampled.

Traditional analysis of well test data usually involves the use of equations derived by Theis (71) and Jacob (72). One of the basic assumptions made in deriving those equations was that all of the water pumped from a well during a pumping or aquifer test comes from the aquifer and that none comes from storage within the well. Since this condition is seldom fulfilled in practice, particularly for the low-yield situations commonly encountered for monitoring wells, these equations are somewhat inappropriate for describing the behavior of water levels during pumping for most monitoring wells.

Popadopulos and Cooper (73) presented an equation describing the discharge from a pumped well which takes into account the volume of water removed from casing storage.

Drawdown values calculated with the relation developed by Popadopulos and Cooper differ significantly from those based on the Theis and Jacob equations. During the early stage of a pumping test a relatively high percentage of discharge comes from casing storage and smaller drawdowns are observed than would be predicted by Theis or Jacob methods. In the later stages of the test a negligible quantity of water is obtained from casing storage and all three drawdown calculation methods produce equivalent results. If the effects of casing storage are not taken into account, it is possible to misinterpret the data and assume an erroneous transmissivity value based on early drawdown data.

Well test data for six monitoring wells studied in Illinois (22) were analyzed using the equations presented by Popadopulos and Cooper. At all of the sites studied, the nonpumping water levels were significantly above the top of the aquifers tapped, suggesting artesian conditions. In this case, a storage coefficient of 0.0001 was used in the analysis of data. The drawdown values described by the Popadopulos and Cooper equation are relatively insensitive to changes in storage coefficient. The storage coefficient values selected therefore should have little effect on the aquifer properties determined at most sites.

Using the Popadopulos and Cooper equations, the percent of aquifer water pumped was calculated for a 2-inch-diameter well at a pumping rate of 500 mL/min for a range of transmissivities and time (see Figure 6-1). Relationships of this type can be developed for any given set of hydrologic parameters to predict the time at which a high percentage of aquifer water would be obtained.

Conducting slug tests on monitoring wells also provides estimates of aquifer transmissivity. Analytical methods described by Freeze and Cherry (68) are recommended for the interpretation of slug test data. Once the transmissivity of aquifers has been determined, the relationships developed by Popadopulos and Cooper can again be applied to predict the quantity of water coming from the aquifer during various phases of pumpage.

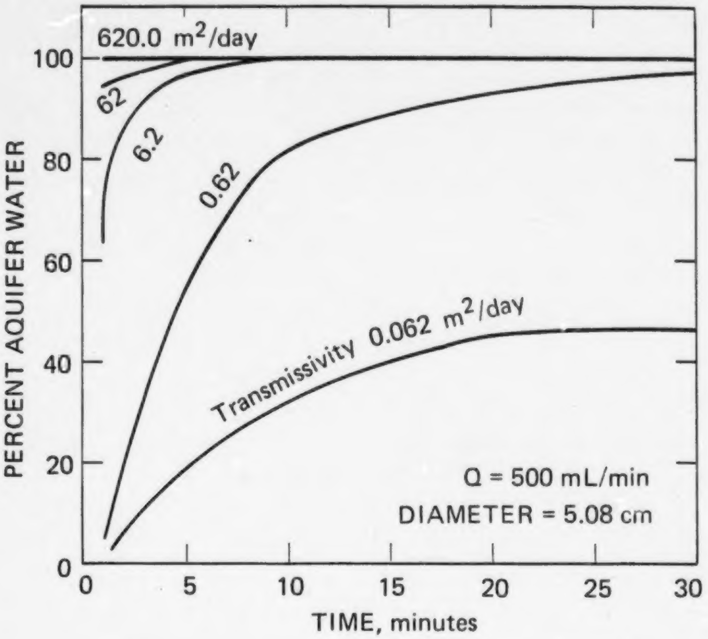


Figure 6-1. Percent of aquifer water versus time for different transmissivities

Based on the studies by Gibb and others (22), the following recommendations are presented for collection of ground-water samples:

1) A brief 2 or 3 hour pumping test should be conducted on each monitoring well to be sampled. Analysis of the pump test data and other hydrologic information should be used to determine the frequency at which samples will be collected and the rate and period of time each well should be pumped prior to collecting the sample. If pumping tests cannot be conducted, slug tests may be substituted to provide the needed hydrologic information.

2) A general rule of thumb of pumping four to six well volumes will, in most cases, produce samples representative of aquifer water. For aquifers with unusually high transmissivities, pumping for periods long enough to remove the "stagnant" water column may induce migration of water from parts of the aquifer remote from the monitoring well. The calculations of percent aquifer water with time provide a more rational basis on which the length of pumping can be determined. Samples should be collected in the minimum time required to produce water representative of the aquifer.

3) A controlled sampling experiment [monitoring indicator parameters (pH, T, Ω^{-1}, and Eh) or collecting samples during an extended period of pumping] should be conducted to accurately determine the chemical quality of aquifer water and to verify the response of the monitoring well to pumping, as predicted from the pump test data. This is best accomplished with an in-line closed measurement cell (74). When the values of the indicator parameters are observed to vary less than ±10% over three consecutive storage volumes, the well may be presumed to have been adequately flushed for representative sampling. Once the chemical character and response of the monitoring

systems have been determined, chemical constituents for routine sampling can be selected.

4) Based on the sensitivity of the selected chemical parameters, a choice of pumps for routine sampling can be made.

5) The monitoring wells should be pumped at a constant rate for a period of time that will result in delivery of at least 95 percent aquifer water. The rate and time of pumping should be determined on the basis of the transmissivity of the aquifer, the well diameter, and the results of the sampling experiment.

6) Measurements of pH, Eh, temperature, and specific conductance also should be made at the time of sample collection. Field determinations of alkalinity together with a mineral analysis, the foregoing measurements and total dissolved solids permit mass and charge balance calculations to be made which are valuable analytical quality control checks.

The steps outlined above are designed for collecting representative samples for inorganic analysis. The same procedures likely will produce representative samples for nonvolatile organic analysis. The use of a syringe sampler (75) in conjunction with pumping or a bottom-draw bailer is desirable for collecting samples for volatile organic constituents.

Special care must be taken to prevent cross-contamination when carrying sampling apparatus from one well to another. The sampling devices must be cleaned thoroughly to ensure that contaminants from one well are not carried to the other. Cleaning procedures should be tailored to the analytes of interest. The use of detergents, dilute hydrochloric acid, hexane, and deionized rinse water often is necessary. In addition, cleaning of sampling devices, all delivery tubes, and tether cables also must be performed thoroughly. The effects of cross-contamination also can be minimized by sampling the least contaminated wells first and progressing to the more contaminated ones. Dedicated sampling devices for each well also may be desirable in certain cases where the potential for cross contamination is high.

In the case of monitoring wells that will not yield water at a rate adequate to be effectively flushed, different procedures must be followed. There are divergent points of view on how flushing should be performed in these situations. The principal difference in the arguments concerns the degree to which such wells should be evacuated. One suggested procedure includes the removal of water to the top of the screened interval to prevent the exposure of the gravel pack or formation to atmospheric conditions (5). Then the sample is taken at a rate which would not cause rapid drawdown. On the other hand, the wells may be pumped dry and allowed to recover. The samples should be collected as soon as a volume of water sufficient for the intended analytical scheme re-enters the well. Exposure of water entering the well for periods longer than 2 or 3 hours may render samples unsuitable and unrepresentative of water contained within the aquifer system. Finally, in these cases, it may be desirable to collect small volumes of water over a period of time, each time pumping the well dry and allowing it to recover. At present there is very little reliable data on which to choose one sampling method over another in "tight" formations.

SECTION 7
EVALUATION OF MATERIALS

The selection of materials used for well construction and sample collection, handling, and storage is a critical consideration in planning the well-conceived monitoring program. The materials of choice should retain their structural integrity for the duration of the monitoring program under actual subsurface conditions. They should neither adsorb nor leach chemical constituents which would bias the collection of representative samples. The material combinations also must be compatible with each other and the goals of the program. For example, in a detective monitoring situation where the presumed inorganic contaminant source (e.g., brine or pickling liquor) is held in a surface impoundment, material selection should be made so as to ensure the reliability of analytical determinations of chemical constituents of the waste in groundwater. These parameters may include pH, specific conductance (Ω^{-1}), alkalinity, hardness, total dissolved solids (TDS), chloride, and trace metals. In this hypothetical situation, the "background" ground water is relatively high in ionic solids, and the goals of a long-term (e.g., 30-year) monitoring program would be most closely met by a properly constructed network of non-metallic or corrosion-resistant monitoring wells. Sampling gear and sample handling precautions also should be chosen carefully to ensure that the samples are neither contaminated nor biased by the effects of materials.

Overview of Subsurface Conditions

The structural requirements for well casings to withstand normal subsurface pressures are met by most common piping materials: steel, polyvinyl chloride, and iron for depths up to ~30 m. In deeper monitoring situations, the use of corrosion-resistant metallic casing of large diameter (>10 cm or 4 inches) may be required to provide necessary structural integrity. Local water well construction practices should serve as a guide.

Metallic corrosion problems may be encountered under either oxidizing or reducing conditions and are aggravated by high dissolved-solids content. Other materials (thermoplastics) may deteriorate under the influence of dissolved chemical substances or direct contact with wastes. Whether the well construction or sampling materials retain their integrity or not, there are also potential problems due to microbial attachment and growth and the sorptive capacity of the exposed materials for the chemical species of interest. Representative sampling depends on the proper choice of materials which can retain their integrity over the entire length of a well casing, from the aerobic, unsaturated surface zone to the unique conditions in the saturated zone.

Chemical Properties of Water and Their Effects on Various Materials

To achieve the goals of a detective monitoring program in a cost-effective manner, one must carefully design and construct the sampling network after consideration of the compatibility of casing and materials with the subsurface environment. If an initial detective network is to be used during the interpretive phase, then the materials should be compatible with probable mixtures of ground water and chemical substances from the source. Compatibility must be judged from a structural and chemical standpoint. Structural considerations are treated in detail in a National Water Well Association manual (18). The main criterion for chemical compatibility should be that the long-term interaction of the casing or sampling materials with the ground water will not cause analytical bias in the interpretation of chemical analysis of the water samples.

For example, assume that a long-term detective monitoring network is to be designed for an acidic metal-plating waste impoundment in a shallow ground-water system where the background water is low in pH and high in dissolved solids. The contaminants of interest are Fe, Mn, Zn, Cr, Cd, and Pb. Under these conditions, it would be imprudent to construct the monitoring wells with black iron or galvanized steel, since inevitable corrosion of the casings would be expected to contribute several of the above metals to the water samples. One may argue that flushing the well will minimize this source of bias or that upgradient and downgradient wells will experience the same degree of interference from corrosion. This argument may hold in some cases; however, the degree of interference in specific wells will depend on the actual conditions at each well site. High background levels of chemical substances contributed by deteriorating well casing might interfere with the analytical determination of the parameters of interest. Very difficult interpretation problems may result if a downgradient galvanized well were at the margin of a plume of acidic waste, and casing corrosion contributed a high "background" of Fe, Mn, Zn, and Cd to water samples drawn from both upgradient and downgradient wells.

In a long-term (e.g., 30-year) detective monitoring program, the judicious selection of casing materials is of utmost importance. The corrosive and leaching properties of ground water over an extended period at a particular site are nearly impossible to predict "a priori." Testing the materials of choice with admixtures of ground water and wastes from a source may be a valuable step prior to the construction of the monitoring well network. If organic contaminants are of concern, it may be necessary to investigate the leaching (or adsorption) of specific compounds at the microgram-per-liter level. In this case, the impact of interfering organic compounds on the separation and analysis of the compounds of interest (e.g., the priority pollutants) may be quite serious. For example, the ubiquity of phthalate esters in flexible plastic (non-polyolefinic) materials and in the environment has caused numerous analytical problems in the determination of many compound classes in natural-water samples (76,77).

The study of the effects of water or aqueous solutions on materials and vice versa presents many obstacles to the investigator. For leaching effects alone, there are at least six critical system variables which must be controlled or considered, including chemical composition of the solution; temperature; rate of flow; composition of the material, its age, pretreatment, and surface area exposed. For purposes of material selection for ground-water monitoring, static or flowing tests with solutions approximating the range of solution composition expected should be sufficient. Protocols for conducting such tests are detailed in several publications (78,79). Additional references have been included in the section which follows along with the performance data available for selected materials.

Candidate Test Solutions for Materials' Evaluation

The composition of ground water or contaminated ground-water solutions varies quite markedly, so there can be no universal test solution applicable to the specific requirements of all ground-water monitoring programs. Tap water or carbonate-buffered distilled water may be a suitable starting point if raw water from the site is unavailable. This is, in effect, what is used in the national certification program of piping materials for potable-water use conducted by the National Sanitation Foundation (80). The chemical composition of leachate and contaminated ground water from investigations of sanitary or hazardous waste landfills provides some composition limits for additional test solutions. Municipal landfill leachate compositions are detailed in a number of publications (11,81). The use of a standardized acetic acid solution has several distinct advantages over a synthesized leachate for testing purposes (81).

Leachate and ground water collected from the vicinity of industrial-waste handling sites are difficult to characterize due to the diversity of sites and wastes involved. However, there are some general indications from the recent literature that two categories of chemical composition predominate. Briefly, from a survey of data from 43 monitoring investigations of hazardous waste sites in the United States, Shuckrow et al. (82) identified high organic/low inorganic and low organic/high inorganic solution compositions as accounting for nearly 44 percent of the sites where ground-water samples were collected. High-inorganic samples contained inorganic constituents at five times the water-quality criteria levels, while low-inorganic samples contained less than the corresponding regulated levels. Similarly, high-organic samples contained greater than 400 micrograms · L^{-1} of individual hazardous organic constituents, while low-organic samples had less than 5 micrograms · L^{-1} of such substances.

Profiles of these two loose categories of contaminated ground-water composition are shown in Table 7-1.

The high-organic group typically exhibited near-neutral pH with TOC and COD levels five to ten times the background values. TDS values were generally two to three times background levels. The four organic compound classes noted below account for 5-32 percent of the TOC. Specific compounds identified in these classes at concentrations exceeding 0.1 mg · L^{-1} include phenols (pentachlorophenol, phenol, nitrophenol);

Table 7-1. Chemical Composition of Contaminated Ground Water Near Hazardous Waste Sites

	High organic/low inorganic		*Low organic/high inorganic*
pH	6-8		3-6
TOC	> 10		-
COD	25-41,000		-
TDS	1,000-2,000		1,000-13,000
Phenols	0.5-3	Zn	1-100
Organic Bases	0.8-25	Cd	1-8
Aromatic Hydrocarbons	0.1-14	Cr	1-200
Chlorinated Aliphatic Hydrocarbons	0.1-150	As	10-10,000

All values in mg·L^{-1}, except for pH
- denotes insufficient data to present a range of values
Source: Reference 82

organic bases (aniline, nitroaniline); aromatic hydrocarbons (benzene, toluene, xylene, substituted benzenes); and chlorinated aliphatic hydrocarbons (dichloroethane, trichloroethane, trichloroethylene, tetrachloroethylene). The presence of these slightly water-soluble compounds in ground water would be expected to affect sorptive or leaching characteristics of the subsurface environment, particularly toward thermoplastic or elastomeric materials.

On the other hand, the low-organic group showed mineral acidity and low pH values. It also was associated with TDS levels five to ten times ambient background. Several metallic elements (Zn, Cd, Cr) normally present in trace amounts were observed at concentrations exceeding background ground-water levels by factors of 10 to 1,000. These low pH, high TDS solutions would be expected to be quite aggressive toward metallic casing materials after extended exposure periods.

It is clear that a reasoned strategy for ground-water monitoring must consider the effects of contaminated water on well construction materials. Unfortunately, there is very little published information on the performance of specific materials in varied hydrogeologic situations. The monitoring strategy must be tailored to fit unique situations, and strict guidelines are currently unavailable.

In the preceding discussion, four categories of subsurface solution conditions were identified. These categories range from carbonate-buffered water to leachate-impacted ground water. The categories are outlined in Table 7-2 with the principal chemical species identified.

The range of chemical exposures represented by these four categories of solution composition should provide general test cases for consideration of compatible well construction materials.

Table 7-2. Solution Composition for a Range of Ground-Water Conditions

General category	*pH*	*Solids content (mg·L⁻¹)*	*Principal soluble species present*
Buffered Weak Acid	5	100-200	Na^+, HCO_3^-, H^+, H_2CO_3 (aq.)
Weak Acid	5	5,000	$RCOO^-$, RCOOH, H^+
Mineral Acid/ High Dissolved Solids	3	1,000-13,000	H^+, Cl^-, $SO_4^=$, Na^+, Ca^{++}, Mg^{++}, transition series and heavy metals
Aqueous Organic Mixture	7	1,000-2,000	Cl^-, $SO_4^=$, HCO_3^-, Na^+, Ca^{++}, Mg^{++} and synthetic organic compounds

R - denotes an organic functional group

Preliminary Ranking of Well Construction/Sampling Materials

A preliminary ranking of commonly used materials was performed on the basis of chemical compatibility and manufacturers' recommendations. Chemical exposures were grouped in one of the related solution categories presented in Table 7-2. A listing of these chemical substances in each category is provided in Table 7-3. Compatibility was judged from the point of view of potential deterioration of each material. No

Table 7-3. Chemical Exposures Grouped in General Solution Categories

Buffered weak acid	*Weak acid*	*Mineral acid/ high dissolved solids*	*Aqueous organic mixtures*
Ammonium Carbonate	Acetic Acid	Acid Mine Waters	Aniline
Ammonium Chloride	Benzoic Acid	Brine Acid	Beer
Calcium Carbonate	Citric Acid	Hydrochloric Acid	Benzene
Aqueous Carbon Dioxide	Glycolic Acid	Metallic Chlorides	Butyl Alcohol
Distilled Water	Fatty Acids	Metallic Sulfates	Carbon Tetrachloride
Potassium Bicarbonate	Formic Acid	Mixed Acids	Chlorobenzene
Sodium Acetate	Gallic Acid	Plating Solutions	Cresol
Sodium Benzoate	Hydrogen Sulfide (aq.)	Seawater	Methyl Alcohol
Sodium Bicarbonate	Lactic Acid	Sulfuric Acid	Methylene Chloride
Sodium Carbonate	Oxalic Acid		Naphtha
Sodium Phosphate	Tannic Acid		Phenol
Sodium Sulfide	Tartaric Acid		Toluene
Sulfite Solutions			Trichloroethylene
			Wine
			Xylene

second-order effects such as adsorption, absorption or leaching were considered. Compatibility ratings were as follows: (3 points) no significant deterioration, embrittlement, or corrosion in general use; (2 points) the potential exists for deterioration, etc., and this material is recommended only after testing; (1 point) the possibility of deterioration, etc., clearly exists and is likely after extended use. Rigid materials used for well casings or sampling gear, as well as semi-rigid or elastomeric materials for tubing and other apparatus, were treated in the same fashion. The compatibility of each material was ranked after the total rating in each category was converted to a percentage of the maximum possible score. The percent ratings in each category served to rank the materials in order, and the sum of the ratings for each material in all four categories provides an overall ranking scheme.

There are limitations in this approach which stem from the lack of detailed information on testing conditions, the subjective nature or varied sources of judgment of "significant" deterioration, and the tenuous relationship of exposures to pure chemicals or dilute aqueous solutions to actual subsurface conditions. However, this preliminary ranking is a starting point for in-depth consideration of materials performance under actual site conditions. Generally recommended materials for monitoring applications are noted by Pettyjohn et al. (17).

The following rigid well-casing materials were considered: PVC I (unplasticized polyvinyl chloride), galvanized steel, carbon steel, Lo-Carbon Steel, Stainless Steels 304 and 316, and Teflon®. Flexible (or semi-rigid) materials commonly used for pump parts, sample transfer lines, in-line devices or storage vessels were rated, including flexible PVC (plasticized), polypropylene, polyethylene (conventional), polyethylene (linear), polymethylmethacrylate (Lucite or Plexiglas), Viton®, silicone, and neoprene. Glass was not considered among the rigid materials due to the unavailability of well screening and hazards associated with its use for casings. Rating results in each category and overall are shown in Tables 7-4 and 7-5 for the rigid and flexible or semi-rigid materials, respectively. Sources for the exposure ratings (83-91) are included in the references.

Table 7-4. Relative Compatibility of Rigid Well-Casing Material

	PVC I	*Galvanized steel*	*Carbon steel*	*Lo-carbon steel*	*Stainless steel 304*	*Stainless steel 316*	*Teflon®**
Buffered Weak Acid	100	56	51	59	97	100	100
Weak Acid	98	59	43	47	96	100	100
Mineral Acid/High Solids	100	48	57	60	80	82	100
Aqueous/Organic Mixtures	64	69	73	73	98	100	100
Percent *Overall Rating*	*91*	*58*	*56*	*59*	*93*	*96*	*100*

*Trademark of DuPont

Preliminary Ranking of Rigid Materials

Teflon®
Stainless Steel 316
Stainless Steel 304
PVC I
Lo-Carbon Steel
Galvanized Steel
Carbon Steel

Table 7-5. Relative Compatibility of Semi-Rigid or Elastomeric Materials

	PVC flexible	*PP*	*PE conv.*	*PE linear*	*PMM*	*Viton®**	*Silicone*	*Neoprene*	*Teflon®**
Buffered Weak Acid	97	97	100	97	90	92	87	85	100
Weak Acid	92	90	94	96	78	78	75	75	100
Mineral Acid/High Solids	100	100	100	100	95	100	78	82	100
Aqueous/Organic Mixtures	62	71	40	60	49	78	49	44	100
Percent *Overall Rating*	*88*	*90*	*84*	*88*	*78*	*87*	*72*	*72*	*100*

*Trademark of DuPont

Preliminary Ranking of Semi-Rigid or Elastomeric Materials

Teflon®
Polypropylene (PP)
PVC flexible/PE linear
Viton®
PE conventional
Plexiglas/Lucite (PMM)
Silicone/Neoprene

Both tables clearly show that superior performance can be expected of the polymeric materials under acidic or high-dissolved-solids conditions. However, as the organic content of the solution increases, one must be prepared for either direct attack on the polymer matrix or more subtle effects due to solvent absorption, adsorption and/or leaching. The only exception to this observation is Teflon®. Provided that sound construction practices are followed, Teflon® can be expected to consistently outperform all other casing and sampling materials. The stainless steels predictably are the most chemical resistant of the ferrous materials. Stainless steel performance may be sensitive to the chloride ion, which can cause pitting corrosion, especially over long-term exposures under acidic conditions. Given the similarity in price, workability, and performance, the remaining ferrous materials provide little advantage for casing/

screen construction. Indeed, the manufacturers' recommendations frequently were contradictory (89,90,91), and as a result, the rankings are essentially equivalent.

The semi-rigid or elastomeric materials ranking in Table 7-5 follows the general chemical resistance expected from manufacturers' recommendations. The "true" polymeric materials — Teflon®, polypropylene, polyethylene, Viton®, silicone, and neoprene — may have an added advantage over polymer formulations (PVC) for rigorous applications since they generally contain fewer extenders, stabilizers, or antioxidants which may cause interferences in analytical determinations. One should be aware of the fact that many flexible materials contain plasticizers, which are potentially troublesome contaminants, especially when industrial solvents are encountered in ground-water systems. The polyolefin materials — polyethylene and polypropylene — are exceptions to this statement since they generally do not contain plasticizers and are more resistant to organic solvent attack than the formulated plastics.

The general rankings provided in the above tables should serve as a basis for preliminary considerations of the suitability of specific materials for ground-water monitoring applications. In the next section, the available literature on actual materials performance in water-handling systems is reviewed for both rigid and flexible materials. This more detailed information is provided in order to permit reasoned considerations of performance in specific applications.

Evaluation of Selected Materials

Since well casing materials are rigid and nonporous, they present a very low surface area to water in the well bore relative to that of the adjacent soil or aquifer particles. There is an extensive body of literature dealing with sorptive interactions of dissolved chemical species in natural waters with solid surfaces. Most of these studies describe the adsorption of trace metals or organic compounds (adsorbates) on mineral particles (adsorbents). Surface area (or particle size) and the organic content of the solid phase are cited almost universally as important variables in the adsorption process. Mineral phases such as quartz (92), aluminum (93), hydrous metal oxides (94), and clays (95), as well as natural sediments (96), have been studied with surface areas ranging from 5 to over 250 $m^2 \cdot g^{-1}$. These active surfaces have been observed to adsorb routinely up to several hundred micrograms of adsorbate per square meter surface area. The applicability of laboratory adsorption experiments to the condensed media of the subsurface is a matter of some controversy (97,98,99,100). However, a simple qualitative comparison of well casing versus subsurface solids should suffice to discount adsorptive interferences from materials selection considerations.

As an example, let us assume that we have constructed a 50-foot (15.3 m) monitoring well with a 2-inch (~5 cm) diameter. The well is screened in the lower 3 feet (1 m) of a 33-foot (10 m) saturated thickness, and the standing water level is 17 feet (~5 m) from the land surface. This hypothetical well bore contains approximately 21 liters of water exposed to about 2 m^2 of casing/screen surface, roughly a 10:1 ratio of water to casing surface. If the solids in the saturated zone were coarse sands with a minimum surface area of 1 $m^2 \cdot g^{-1}$, the casing water volume would have been exposed to at least 10^4 m^2 of solid surface! If we presume that the casing has been in place long enough to equilibrate with subsurface conditions, we may expect that the surface activity of the coatings (microbial slimes, organic films, or micro precipitates) on neighboring particles and the casing material would be roughly equivalent. Thus, the occurrence of adsorptive bias in our representative water sample, taken after purging the stored volume, would be likely only if the well casing presented an extremely active surface uncharacteristic of nonporous materials and if the rates of desorption/adsorption were very fast relative to the duration of a sampling operation.

Although reports on the rates of adsorption and desorption in aqueous solution are sparse, most workers have employed at least a 4-hour equilibration period in laboratory studies. Reported half-times for maximum adsorption of metals and nutrients are in the range of 0.5-2 hours (27,29,54). These times are much greater than the time necessary to sample most monitoring wells after the removal of stagnant water from the well bore. On this basis, the potential bias effects due to adsorptive interactions with well casings may be discounted. Such effects would be far more critical in sample transfer and storage procedures prior to separation or analysis. A note of caution should be added with regard to the absorption of organic solvents by polymeric materials. Past exposures of casing or tubing surfaces to high aqueous organic mixtures may cause the migration of organic solvents into the polymer matrix. Normal cleaning procedures may not be sufficient to remove this potential source of contamination in succeeding samples. Also, freshly cleaned materials may represent active surfaces for sorption or leaching effects.

Teflon® Well Casing

Teflon® represents a nearly ideal well construction material. Inertness to chemical attack, poor sorptive properties, and low leach potential are clear advantages of rigid-Teflon® PFA for well screen and casing. However, these advantages are rather expensive in comparison to other materials. Where situations allow, using Teflon® casing and screen in the saturated zone with another suitable material as the upper casing may be a viable, less-expensive alternative (17). The structural properties of Teflon® are sufficient for the most exacting environments, and this factor gives it a clear advantage over glass. Teflon® has not been reported to contribute organic or inorganic contaminants to aqueous solutions.

Stainless Steel Well Casing

Stainless steel has been the material of choice for casing and screen when subsurface conditions require a durable corrosion-resistant material. In the preliminary materials ranking, 316 Stainless showed a slight edge over type 304. The principal compositional difference between the two types is the inclusion of 2-3 percent molybdenum in type 316 (101). The molybdenum content gives 316 Stainless improved resistance to sulfur-containing species as well as sulfuric acid solutions. Resistance to oxidizing acids is somewhat poorer than other chromium-nickel steels; however, reducing conditions are more frequently encountered in well-casing applications. The 316 Stainless Steels are less susceptible to the pitting or pin-hole corrosion caused by organic acids or halide solutions. They are the materials of choice in industries where excessive metal contamination of process streams must be avoided (e.g., pharmaceuticals). Provided that surface coating residues from manufacture or storage are removed, stainless steel well casing, screen, and fittings can be expected to function nearly as well as Teflon® in most monitoring applications. Chromium or nickel contamination may result after long exposure to very corrosive conditions; however, physical failure of the casing would probably accompany or precede such an occurrence. Proper well flushing prior to sampling should be sufficient to minimize problems with these materials (102). Details of well-executed monitoring efforts in which stainless steel well casing and screen have been used successfully are provided by several recent publications (38,103,104).

PVC Well Casing

Polyvinyl chloride (PVC-Type 1) thermoplastic well casing is composed of a rigid unplasticized polymer formulation with many desirable properties for monitoring well construction. It is a rigid material with very good chemical resistance except to low-molecular-weight ketones, aldehydes, and chlorinated solvents. The preliminary ranking in the previous section establishes PVC as a close second to Teflon® and 316 Stainless Steel with respect to resistance to acid solutions, and it may be expected to outperform any of the ferrous materials in acidic environments of high ionic strength. There may be potential problems when PVC is used in contact with aqueous organic mixtures or under conditions which might encourage leaching of substances from the polymer matrix. It should be noted that manufacturers do not recommend the use of threaded schedule 40 PVC casing because of potential mechanical failures. Schedule 80 threaded PVC well casing is sufficiently durable for most well construction applications.

PVC product formulations and applicable standards

There are few piping materials that have received the scrutiny to which PVC products have been subjected. Discussions of durability, health effects of leachable components, and modes of fabrication have gone on since U.S. commercial production began in the 1940's (105). A number of standard specifications exist covering PVC well casing (106,107,108,109), which is tested by the National Sanitation Foundation (NSF) using a protocol equivalent to that for all plastic pipe used in potable water applications (80). In general, the chemical resistance of polymeric materials is improved by the incorporation of fewer ingredients in the formulation (88), and unplasticized PVC bears this out in tests of weatherability (110).

There have been many concerns voiced about the release of vinyl chloride monomer from PVC products. Process control technologies have significantly reduced the total residual vinyl chloride monomer (RVCM) levels in the resin and finished products. In fact, the NSF chemical, taste, and odor testing protocol (67) limits the levels of RVCM to ≤ 10 ppm in NSF-listed products. This level of residual monomer limits the potential leached concentrations to 1-2 micrograms $\cdot$ L^{-1}. From 1977 to 1980, the RVCM failure rate in NSF tests of PVC formulations fell from 9 percent to less than 1 percent (111). It would be expected that the leachable amounts of vinyl chloride monomer decrease as the total RVCM levels in products are reduced. This has been borne out in several laboratory and field studies which demonstrate that vinyl chloride monomer (VCM) does leach into potable water at the low ppb level as a result of prolonged solution exposures. For example, an EPA field study of five potable water supplies with plastic pipe manufactured between 1964 and 1975 showed VCM levels between 0.03 and 1.4 microgram $\cdot$ L^{-1} (43). The higher levels observed were from samples taken from more recently constructed installations. Levels of VCM leached into water from static or flowing tests have been shown to be a function of exposed surface area and actual levels of RVCM in the product (42,112,113). These laboratory results on samples that meet NSF Standard 14 specifications (80) show that leached VCM levels are in the <1 to 2 microgram $\cdot$ L^{-1} range. Though these levels are below those of toxicological concern (111) the potential exists for organic analytical interferences in monitoring situations where prolonged exposure to aggressive aqueous organic mixtures may occur.

Rigid PVC materials used for pipe and well casing with NSF-listing are essentially free of plasticizers. Although plasticizers are unnecessary for rigid pipe applications, a small number of sources of well casing may include plasticizers which are added along with the thermal stabilizer component. Plasticizer levels in such pipe samples would not be expected to exceed 0.01%. These levels are far lower than those in flexible PVC formulations for tubing or sheet materials which can contain up to 30-50 percent by weight of plasticizer. Rigid PVC contains several types of other additives at levels approaching 5 percent by weight, which may pose a source of bias or analytical interferences in ground-water monitoring programs (113). These additives include pigments, antioxidants, thermal stabilizers, and inorganic fillers (114,115). Some representative chemical classes of additives which have been used in rigid PVC manufacture are contained in Table 7-6. There are clearly many possible combinations of substances which may be included in PVC formulations. The potential for their release into aqueous solutions or ground waters may be determined by the individual formulation, rigor of exposure, manufacturing techniques, and the chemical state of a particular component in the finished product. Here again, NSF-listed products for well casing and potable water applications are continually checked and tested. Products that are found to exceed the maximum contaminant levels set by the National Interim Primary Drinking Water Standards in leach tests (Table 7-7) do not qualify to carry the NSF logo. Their use should be avoided in monitoring well construction since many manufacturers include compounding ingredients that are not permitted by the specifications.

Table 7-6. Representative Classes of Additives in Rigid PVC Materials Used for Pipe or Well Casing

(Concentration in wt. %)

Heat stabilizers (0.2-1.0%)

- Dibutyltin diesters of lauric and maleic acids
- Dibutyltin bis (laurylmercaptide)
- Dibutyltin-β-mercaptopropionate
- di-n-octyltin maleate
- di-n-octyltin-S,S'-bis isoctyl mercaptoacetate
- di-n-octyltin-β-mercaptopropionate
- Various other alkyltin compounds
- Various proprietary antimony compounds

Fillers (1-5%)

- $CaCO_3$
- diatomaceous earth
- clays

Pigments

- TiO_2
- carbon black
- iron and other metallic oxides

Lubricants (1-5%)

- stearic acid
- calcium stearate
- glycerol monostearate
- montan wax
- polyethylene wax

(Reference 115)

Table 7-7. Chemical Parameters Covered by NSF Standard 14 for Finished Products* and in Standard Leach Tests

Parameter	*Maximum contaminant level ($mg \cdot L^{-1}$)*	
Antimony (Sb)	0.05†	0.05†
Arsenic (As)	0.05	
Barium (Ba)	1.0	
Cadmium (Cd)	0.01	
Chromium (Cr)	0.05	
Lead (Pb)	0.05	
Mercury (Hg)	0.002	
Phenolic substances	0.05†	
Residual vinyl chloride monomer* (RVCM)	10†	
Selenium (Se)	0.01†	
Tin (Sn)	0.05	

† Not covered under National Interim Primary Drinking Water Regulations.
* Total residual after complete dissolution of polymer matrix.

Tabulated values are the maximum levels permissible in NSF-listed products after standardized leach testing in weakly acidic aqueous solution. [Carbonic acid solution with 100 $mg \cdot L^{-1}$ hardness as $CaCO_3$ with 0.5 $mg \cdot L^{-1}$ chlorine; pH 5.0 to 0.2; and surface to solution ratio of 6.5 $cm^2 \cdot mL^{-1}$]

Source: National Sanitation Foundation

Practical considerations and potential for analytical bias due to use of PVC well casing

The use of NSF-listed well casings provides us with a minimum standard material that can be judged for suitability in specific monitoring situations. All types of well casings should be cleaned with detergent and rinsed with water prior to well construction to remove processing lubricants and release agents. This is particularly true of PVC well casing, which may be coated with natural or synthetic waxes, fatty acids, or fatty acid esters.

Threaded joints are the preferred means of connecting sections of PVC well casing. In this way, problems associated with use of solvent primers and cements can be avoided. Threaded joints on PVC well casing (or pipe) can be provided in three ways: solvent cementing a molded thread adaptor to the end of the pipe, molded flush-threaded joints built into each pipe section, and cutting tapered threads on the pipe with National Pipe Thread sized dies. The latter method is only recommended by the industry for schedule 80 PVC well casing or pipe. Numerous studies have pointed out analytical interferences and direct sources of bias caused by the migration of the components of solvent mixtures into water samples (79,41,116,117). The mixtures frequently contain two or more of the following solvents: methyl-ethylketone (2-butanone), methyl-butylketones, cyclohexanone, tetrahydrofuran, and dimethylformamide. Some of these substances may not be among the analytes of interest; however, their presence in a water sample can cause severe problems in the determination of priority pollutants (41). In the experience of the Illinois State Water Survey, even minimal solvent-cement application is sufficient to supply consistent levels of cement/primer components above 100 ppb in actual ground-water samples despite proper well development and flushing prior to sampling. This problem may persist for months after well construction even after repeated attempts to develop the wells. Prolonged exposure to aggressive aqueous mixtures is probably the single most important factor contributing to leaching problems. This situation is decidedly different from the high-volume flow-through testing conditions employed for PVC plumbing for potable water transport applications. There are various alternative joining procedures for PVC pipe other than solvent cementing or threaded joints. These include: twist-lock or spline unions which employ O-ring seals. For these procedures the integrity of the ring material must also be considered in evaluating appropriate materials for well casings.

Other sources of potential bias from the use of PVC well casing may arise from the additives present as compounding ingredients, such as those in Table 7-6. These substances are added to color the pipe, protect it from oxidation or exposure to sunlight and aid in the maintenance of the integrity of the virgin resin in extrusion or molding. For example, thermal stabilizers such as the organotin compounds (e.g., dimethyltin-bis-isooctylthioglycolate) are added to scavenge HCl released when the resin is heated. Liberated HCl would otherwise attack the polymer matrix and degrade the product. Ideally, minimal amounts of such substances should be added to insure product integrity. In practice, however, it is difficult to determine ideal additive concentrations and an excess may be present in most finished products. Therefore, the initial compounding ingredients, as well as the products of their reaction with species generated during processing or use, the ingredients themselves, and the polymer matrix, must be considered among the species that may leach or migrate from the finished product.

At present there are very few data available on the identity and concentrations of chemical species leachable from PVC pipe under actual subsurface conditions. Metallic and organometallic compounding ingredients have received the most attention in the literature due mainly to the ease of spectroscopic metal determinations relative to that of specific organic compounds. Specific organic compound determinations are difficult since both the mixtures of original ingredients and their reaction products are present in a solid matrix which is more or less insoluble (114-118).

Lead and cadmium compounds are not permitted as compounding ingredients in U.S.-manufactured, NSF-listed PVC well casing. There are a series of papers from the United Kingdom which demonstrate various aspects of the leaching process for rigid PVC materials stabilized with lead stearate or tribasic lead sulfate (78,119,120). In this comprehensive study, R. F. Packham detailed the equilibration of lead-stabilized rigid PVC over a range of pretreatment, aging, and leach-solution conditions. His conclusions include the following points: 1) total Pb content was not simply related to the quantity extractable, although surface area was an important variable (he also noted significant variations along a length of pipe and the consequences of proportionately longer heat exposure for larger-diameter pipe); 2) the bulk of the extractable Pb seemed to be present in a surface-rich layer ($\sim 30 \text{ mg} \cdot \text{Pb} \cdot \text{m}^{-2}$), which could be removed by abrasion, ethanolic-NaOH or oxidizing acids; 3) pre-exposure of rigid PVC to organic acids, organic mixtures, and trichloroethylene actually increased the amounts of Pb extracted by the standard bicarbonate solution; 4) even after removal of the surface layer, additional leachable Pb could be attributed to a slow diffusion process of the order of $0.2 \text{ mg} \cdot \text{Pb} \cdot \text{week}^{-1} \cdot \text{m}^{-2}$; and 5) there was some indication that lead stearate stabilizers would support higher leachable lead quantities than inorganic tribasic lead sulfate. This study significantly supplemented the earlier work of Niklas and Meyer (121). The results of this work clearly show some of the important variables involved in the leaching of compounding ingredients from rigid PVC well casing. Pretreatment and cleaning, aging, and the effects of multiple extractions (static or flowing test conditions) are factors which should be considered in PVC well-casing applications. Actual field conditions may either decrease or increase the long-term release of compounding ingredients (81) through surface area effects, and the chemical species of interest must be carefully considered.

In more recent work, Boettner et al. (40) studied the release of alkyltin species from PVC pipe stabilized with dialkyltin-bis-isooctylthioglycolate compounds. Their results clearly showed that levels of leachable organometallics were of the order of 10-50 ppb on initial exposure to chlorinated, buffered, pH 5 carbonic acid solution. Concentrations of leachable tin due to successive exposures gradually decreased in a biphasic manner for up to 3 weeks. The actual mobile tin species were not identified; however, there was an indication that they were ionic in nature. The leaching of related tin compounds from coatings is recognized to be a complex process which may occur from an active fraction of the exposed area (122) and is certainly affected by the chemistry of individual species (123). The leaching process is an active area of research which will prove most helpful in the interpretation of chemical investigations of materials effects in many environmental applications. Though the tin or antimony compounds used as stabilizers are rarely of interest for monitoring, their impact as analytical interferences and/or sources of bias must be carefully considered.

The bulk of the data available on PVC chemical resistance and leaching strongly suggests that there are potential pitfalls involved in the use of PVC well casing in situations where trace chemical species are of interest. At this time, it is clear that PVC exposed to aqueous organic mixtures has the potential to act as a source of foreign organic or metallic compounds in excess of what may occur in predominantly inorganic solutions. Detailed monitoring efforts for organic compounds at the microgram $\cdot$ L^{-1} level may be significantly biased by the sole use of PVC well casing, particularly during the initial study period. Thereafter, the slow diffusive release of PVC additives may be expected to continue for some time. Whether or not these effects significantly bias monitoring results will depend on specific conditions and the actual formulations used. Caution is indicated from the available data on these processes.

The potential for solvent absorption, and the adsorptive uptake or release of organic compounds and metals by PVC pipe, has been discussed by several authors (39). However, there are few data documenting this potential under field conditions. The mechanism for solvent-cementing lies in the absorption of the solvent and partial dissolution of the PVC matrix to produce a "solvent-weld." Therefore, the exposure of PVC to low molecular ketone, aldehydes, acids, amides, chlorinated alkenes or alkanes may cause the actual degradation of the polymer matrix and/or the release of compounding ingredients which otherwise would remain in the solid. The concept of discrete adsorption "sites" on PVC which may be expected to equilibrate with stored water in monitoring wells (124) may be applicable to certain situations, though the inevitable adsorption of natural organic matter and microbial coatings argue against any specific adsorptive interaction. If circumstances do not permit the use of a more appropriate material (e.g., Teflon®, stainless steel) under high-organic or unknown conditions, then at least several paired wells should be constructed of a non-polymeric material and PVC. This will allow at least an order-of-magnitude determination of the potential bias due to PVC well casing.

Further, manufactured casing and screen is preferable to off-the-shelf PVC pipe. The practice of sawing slots in the pipe (e.g., home-made screens) should be avoided since this procedure exposes fresh surfaces of the material, increasing the risk of releasing compounding ingredients or reaction products. Also, it is very difficult to properly slot casing materials by sawing operations.

Casing Made from Other Ferrous Materials

Ferrous metal well casing and screen materials, with the exception of stainless steels, include carbon steel, low carbon or copper (0.2%) steels, and various steels with a galvanized coating. In the preliminary ranking contained in Table 7-4, these materials ranked consistently poorer than Teflon® and stainless steels. They do, however, show an advantage over rigid PVC in exposures to aqueous organic mixtures. The carbon steels were formulated to improve resistance to atmospheric corrosion. To achieve this increased resistance, it is necessary for the material to undergo alternate wetting and drying cycles. For non-coated steels buried in soils or in the saturated zone, the difference between the corrosion resistance of either variety is negligible (125). Both carbon- and copper-steel well casings may be expected to corrode, and corrosion products may include oxides of Fe and Mn (and trace constituents), as well as various metal sulfides. Under oxidizing conditions, the principal products are solid hydrous oxides of these metals, with a large range of potential particle sizes. The solids may accumulate in the well screen, at the bottom of the well, or on the casing surface. The potential also exists for the production of stable colloidal oxide particles that can pass through conventional membrane filtration media (126). Reducing conditions will generally provide higher levels of truly dissolved metallic corrosion products in well storage waters (127,128). Galvanized steels are protected by a zinc coating applied by hot dipping or electroplating processes. The corrosion resistance of a galvanized steel is generally improved over conventional steels; however, the products of initial corrosion will include iron, manganese, and zinc (and trace cadmium) species which may be among the analytes of interest in a monitoring program.

Corrosion products from conventional or galvanized steels represent a potential source of adsorptive interferences. The accumulation of the solid products has the effect of increasing both the activity and the exposed surface area for adsorption, reaction, and desorption processes. Surface interactions can thereby cause significant changes in dissolved metal or organic compound concentrations in water samples (102). Flushing the stored water from the well casing may not be sufficient to minimize this source of bias because the effects of the disturbance of surface coatings or accumulated products in the bottom of the well would be difficult, if not impossible, to predict. In comparison with glass, plastic, and coated steel surfaces, galvanized metal presents a rather active surface for adsorption of orthophosphate (29). The age of the surface and the total area of exposure have been found to be important variables in the adsorption process; however, adsorption is not a linear function of galvanized-metal surface area.

Field data for conventional and galvanized steels provide additional reasons for caution in their use for well casings or screens. The water well industry routinely chooses alternative nonconductive or corrosion-resistant materials in areas where normal groundwater conditions are known to attack the common steels. In fact, regional or local practices in the selection of water well construction materials provide valuable preliminary guidelines, for routine monitoring efforts.

The preliminary ranking of ferrous materials in the previous section is well supported by available monitoring data. Results from studies of the glaciated terrain of Maine demonstrate that water samples from steel production wells used for monitoring consistently showed Fe and Mn levels 30-50 times higher than those of samples from adjacent PVC monitoring wells finished at the same depth (129). In thess data, water sample composition (DO, T, and TDS) was remarkably similar, with the exception of iron and manganese levels. Again, though iron and manganese may not be among the parameters of interest in a specific situation, the presence of their metallic oxides or soluble complexes may interfere with the determination of other metals. This source of bias may be particularly serious in unfiltered samples which cannot be preserved properly in the field.

Galvanized steel well casing and screen may seem to be a less costly alternative to the use of more appropriate materials (e.g., Teflon®, stainless steel, PVC) in saturated, high-dissolved-solids environments since it corrodes less rapidly than conventional steels (130,131). Under reducing conditions at pH values between 5 and 7, the presence of chloride, carbonate, and nitrate can encourage rapid aggressive attack of the material. In some cases, $CO_3^{=}$ and NO_3^{-} may actually reverse the electrochemical potential between the zinc oxide coating and the base metal, resulting in accelerated dissolution of the iron pipe. Sulfur compounds, organic compounds, and dissolved copper concentrations also are implicated in the rapid deterioration of galvanized steels under saturated conditions. Monitoring data from wetland soils and bog environments disclose that galvanized materials are a liability in ground-water investigations. Instances of casing or screen dissolution under these conditions resulting in zinc concentrations approaching 10 ppm are common (38,132,133). In these cases, water samples from PVC and stainless steel monitoring wells showed zinc concentrations 1-2 orders of magnitude below those observed in samples from adjacent galvanized steel wells despite the fact that comparable well flushing techniques were used. This is consistent with the dissolution and migration of zinc from galvanized monitoring installations, providing an additional source of bias that careful flushing does not minimize.

It appears, therefore, that in corrosive environments, galvanized steel presents little or no advantage over conventional steels, and more appropriate materials should be considered. Some degree of compromise may be achieved by casing the upper unsaturated zone with steel casing and then using PVC, stainless, or Teflon® casing and screen in the saturated zone. However, the potential for abrasion during sampling operations or galvanic corrosion effects should be evaluated prior to installation.

Pumps Used in Development

The large variety of centrifugal, peristaltic, impeller, and submersible pump designs precludes an in-depth discussion of their potential effects on the results of ground-water monitoring efforts. According to the situation, one must carefully consider the compatibility of the materials found in high capacity pumps with subsurface conditions. The methodology of monitoring well development is probably far more critical in this respect than the pumping mechanism or water-contacting materials. One of the most serious problems arises in the use of water of poor or indeterminate quality for surging or jetting operations. This water can migrate into the formation of interest and alter local aquifer properties. Exhaustive pumping of a well after development to determine hydraulic conductivity from time-vs-drawdown or recovery curves should be sufficient to minimize this problem.

Special precautions may be called for in severely contaminated areas and where flammable or toxic materials are present in ground water. In these cases, a plan for the management of water (as well as cuttings) extracted during drilling or development should be designed. All such operations should be carefully supervised by the chief field engineer or scientist. The practice of returning contaminated water to the formation is strongly discouraged since there is no tested procedure to account for changes which occur during surface storage or mixing.

Grouts, Cements, Muds, and Drilling Fluids

Various drilling aids, cements, and sealant formulations are used to achieve two main goals: to maintain an open borehole in rotary and cable tool operations in unconsolidated formations, and to effect a seal between the surface or overlying formations and the casing/screened intervals so that runoff or other sources of water do not enter the well bore. Problems involved in obtaining representative water samples stem mainly from the persistence of drilling aid components and the long-term integrity of grouts or cement seals.

Drilling aids

For the most part, water-based drilling fluids are used in freshwater applications where the total-dissolved-solids content of ground water is below 10,000 mg $\cdot$ L^{-1}. The fluids are introduced for several purposes, including cooling and lubrication of the bit, suspension and removal of cuttings, stabilization of the borehole by building up a cake on the sides of the hole, and minimization of formation damage due to water loss or penetration of solids. Freshwater muds are formulated mainly in three types: 1) bentonite, attapulgite or clay-based muds with pH adjusted to 9-9.5 with caustic; 2) polymer-extended clay (organic) muds; and 3) inhibited clay muds which utilize lignosulfonates or lignin to counteract the effects of contaminants which would otherwise destabilize the slurry and prevent effective cutting removal. The first two types are used most frequently in water-well drilling applications (134). Both of these main types of mud formulations and a spectrum of combined compositions have been used for the construction of monitoring wells. The basic ingredients in a drilling mud are shown in Table 7-8, and the main distinction between bentonite and organic muds is the addition of natural or synthetic organic polymers to adjust consistency, viscosity, or surface tension.

For monitoring applications, there are distinct advantages to augering, air-rotary, or clear-water rotary drilling techniques where conditions permit. The desired approach is the least possible introduction of foreign materials into the borehole. Compressor lubricants for air-rotary rigs may rule out this method for trace organic monitoring work although filters are available to minimize such problems. In geologic situations where water-based drilling fluids are a necessity, the predominantly inorganic clay muds are preferable over those containing organic materials, since the introduction of

Table 7-8. Components of Well-Drilling Fluids

Functional class	*Examples*
Inert solids	calcium and barium sulfates
Inorganic salts	sodium chloride
Active solids	bentonite (~90% Na-montmorillonite clay), attapulgite, calcium carbonate
Bactericides	formaldehyde, hypochlorite
Organic polymers	partially hydrolyzed polyacrylamide, corn or bean starch, carboxymethylcellulose, copolymers of acrylamide and sodium acrylate, lignosulfates/lignin

(References 57, 134, 135, 136)

substrates for microbial activity can seriously impact the integrity of water samples (57,58). The decomposition of the organic components of drilling muds may be expected to be a function of their chemical structure, microbial populations, the presence of nutrients, and various physical and chemical factors controlling the distribution of organic substances in the subsurface. Studies to date have been confined primarily to oil or gas drilling operations in marine or subarctic regions where permafrost impacts have been investigated (137,138).

Comprehensive freshwater drilling studies of the persistence of organic additives are sparse; however, Brobst and Buszka (59) have investigated the problem using chemical oxygen demand (COD) as an indicator of the organic mud. In this study, monitoring wells were constructed by rotary methods using various clay and organic muds. Since background COD levels were in the range of 2-10 mg $\cdot$ L^{-1} and the drilling muds of interest were in the range of 1-10,000 mg $\cdot$ L^{-1}, COD was a reliable indicator of persistent analytical bias. Their results show that, despite careful well development and flushing prior to sampling, COD levels from mud-drilled wells were consistently 3-10 times higher than the background levels measured in adjacent wells. Somewhat longer persistence was noted for bentonite muds as compared with organic muds, and the effectiveness of supplements to speed organic decomposition was not uniform. The effects were found to persist from 20 to 120 days after well completion.

The potential consequences of using drilling aids should be obvious. Although COD is a surrogate parameter for a number of reduced inorganic and organic chemical species, levels 3-10 times background can be expected to seriously bias analytical results in ground-water monitoring programs. Filtration or well flushing prior to sampling may not be sufficient to reduce mud-related bias. The stable colloidal-sized particles in some muds will readily form emulsions in organic solvent extraction procedures. The addition of large amounts of organic substrate for microorganisms into the subsurface will have the effect of lowering the oxidation-reduction potential, perhaps drastically shifting both the chemical and biochemical processes in the vicinity of the well bore. Since organic decomposition processes will depend largely on microbial activity, there may be significant differences in the dominant pathways, rates, and products from installation to installation. It is also most unlikely that biocides, enzyme supplements, or chemical oxidants (hypochlorite) will totally ameliorate the situation. An additional word of caution should be added against the return of mud-contaminated cuttings to the borehole, since this will only increase the amoun[illegible]oreign material in the vicinity of the sampling interval.

Seals, grouts, and cements

Seals, grouts, and cements are the primary safeguards against the migration of water from the surface and from overlying or adjacent formations into monitoring wells. Surface seals also must be completed with concern for the security at the wellhead by including casing sheaths and locking caps. Most seals between the formation of interest and regions above or below are made by the addition of clay materials or cement. Bentonite clay can swell from 10-15 times in volume after wetting with deionized water. Variations in the composition of the contacting solution can severely reduce the swelling of clay seals. Swelling volumes of 25-50 percent of the maximum values are not uncommon. The organic content of the solution in contact with the clay can have a dramatic effect on the integrity of the seal. Organic compounds can cause significant disruption of normal shrinking, swelling, or dehydration of the clay lattice during alternate wetting and drying cycles (139). Alcohols, ketones, and other polar organic solvents have a significant potential for these changes. On the microscopic level, these phenomena can materially increase the permeability of the clay seal. This is presently an active area of research which has wide application in well construction, landfill liners, and slurry or grout cutoff walls (56,140). Macroscopic changes in the permeability of clay or cement seals can occur due to solution channeling by aggressive solvents, compaction or subsidence, and freezing and thawing processes at the surface.

Chemical-resistant and expanding cement formulations effectively minimize these problems. Faulty seals or grouts can seriously bias the analytical results on water samples from the formation of interest, particularly if water quality conditions vary or surface soils are badly contaminated. The impact of leaking seals may go far beyond the realm of analytical interferences or non-representative samples. A leaky well bore may act as a conduit to permit rapid contaminant migration which otherwise would not have occurred. This is one aspect of a ground-water monitoring program which should not be left to an unsupervised drilling crew or last-minute substitutions for preferred materials.

Evaluation of Sample Collection Materials

The choices of sample collection devices, procedures, and all materials which ultimately contact water samples are probably the most critical considerations in a ground-water monitoring program. The materials' related problems which may be encountered in well construction are secondary to those involved in sample handling. The careful monitoring program planner must evaluate the potential of collection mechanisms and all materials which contact the samples to introduce interference or bias into the final analytical result. For example, a collection mechanism that creates turbulent transfer of the sample and the opportunity for gas exchange (e.g., air-lift pumping mechanisms) is clearly inappropriate in sampling for volatile organic compounds and pH- or redox-sensitive chemical species. The act of sampling alone would alter solution composition, introducing bias into subsequent analytical determinations as well as matrix effects which may not be totally accounted for by spiked field samples.

Desirable attributes for sample collection materials include:

1) Durability, reliability, and ease of repair
2) A minimum number of moving parts or combinations of materials

3) Capability of being cleaned and sterilized effectively to prevent cross-contamination between sampling points
4) Capacity for being checked for deterioration or malfunctions such as stuck check valves, clogging, and breakage
5) Verified low potential for introducing contamination, bias, or interferences into the analytical results

Each of these attributes plays an important role in the overall performance of monitoring efforts and bears directly on the successful retrieval of respresentative water samples. The difficulties involved in the evaluation of materials for sample collection apparatus stem mainly from the variety of combinations of components in pumps (or other samplers) and the properties of polymeric and elastomeric materials for tubing or transfer lines.

Sampling devices

Apart from the actual mechanisms employed by sampling devices, the consideration of materials is of prime importance in the choice of a suitable sampler. Fortunately, most types of devices are constructed in several models which may be chosen for specific monitoring situations. For example, bailers are presently fabricated by commercial suppliers in Teflon®, stainless/Teflon®, stainless/PVC 1, and totally PVC 1. These materials satisfy the major critical materials' specifications. Problems arise in materials selection with samplers employing non-rigid components. Even those devices which incorporate a single pair of 0-rings may be limited in their application by the material employed.

The preliminary ranking of materials in Tables 7-4 and 7-5 serves as a general guide for materials selection for sampling devices. Teflon® again incorporates most of the characteristics for an ideal material in sampling applications. However, it is a difficult material to machine and threaded components are very easily damaged. For chemical resistance and durability, several materials other than stainless steel may be expected to perform satisfactorily in low-organic environments. These materials include polypropylene, linear polyethylene, plasticized PVC, Viton®, and conventional polyethylene. Viton® is a preferred material for elastomeric parts, since it may be expected to give improved chemical resistance over silicone and neoprene.

One may expect that the least desirable material in a given sampler design will eventually cause monitoring problems. For example, significant differences have been observed in the organic contamination potential of impeller pumps as a function of impeller material (3). In this instance, consistently high PCB (polychlorinated biphenyl) values due to cross-contamination were observed in samples obtained by a plastic impeller pump relative to those obtained from a device with a stainless steel impeller. Similarly, solvent cements used in the construction of rigid-PVC bailers can result in gross analytical errors for volatile organic compounds (41) in samples collected shortly after bailer fabrication.

Flexible materials in collection devices can be particularly problematic since they owe their flexibility and resiliency to plasticizers as well as a range of compounding ingredients no less diverse than those contained in Table 7-6 for polyvinyl chloride. Here, a considerable overlap between materials selection for samplers and tubing or transfer lines arises. Careful consideration should be given to flexible components of diaphragm, bladder, or peristaltic pumps based on the discussion in the next section. The intimate contact of water samples with tubing materials requires that absorption, adsorption, and leaching potential be carefully considered for specific materials in monitoring applications. True polymeric materials like the polyolefins may be expected to cause fewer problems than formulations or "sandwich" materials.

Tubing and transfer lines

Tubing and transfer lines are available in a variety of polymeric or elastomeric materials. Certain applications (e.g., peristaltic or bladder pumps) demand a high-resiliency material, and it may be necessary to sacrifice chemical resistance to achieve the desired structural performance. The bulk of common tubing materials, with the exception of Teflon®, contain a wide range of additives. In addition to the major classes of additives in Table 7-6, plasticizers, lubricants, antistatic agents, tackifiers, and other ingredients may be present in flexible synthetic materials (115). In general, true polymers (e.g., polyolefins like polyethylene and polypropylene) contain far lower amounts of such ingredients. Formulations change frequently as manufacturers strive to keep production costs low, so a particular material may show significant variation from lot to lot. Plasticizers are frequently present at levels between 15 and 50 percent of the total weight of flexible products. As a result of this fact and widespread plastics usage, major plasticizers, such as phthalate esters, have been consistently identified in environmental samples.

There are numerous lab and field studies which detail the contamination of water samples by contact with plastic tubing. Plasticized PVC is a particularly problematic material in this respect, showing a high potential for both the absorption/release of organic compounds (3), and the leaching of compounding ingredients (49,141). By these mechanisms, PVC tubing may contribute to cross-contamination between sampling points as well as directly bias the determination of several classes of priority pollutants. Several studies have reported data that illustrate such interferences, particularly due to the presence of phthalates (142,143). Table 7-9 shows the frequency occurrence of phthalate esters in industrial wastewaters (144) and ground-water samples. A comparison of the frequency levels at similar analytical sensitivities from USEPA monitoring in the "Superfund" program (145) and those from the New York State study (143) relative to that in industrial wastewaters is quite revealing. Careful sampling and analytical quality assurance procedures drastically reduce the overall frequency of detection. This

Table 7-9. Frequency of Occurrence of Phthalate Esters in Wastewater and Ground-Water Samples

Phthalates	*Industrial wastewaters*	*N.Y. state public water supply wells*	*"Superfund" monitoring samples*
bis-(2-ethylhexyl) phthalate	42%	98%	0%
Dibutyl phthalate	19	72	4.8
Diethyl phthalate	8	35	1.9
Butylbenzyl phthalate	8	26	<1
Dioctyl phthalate	6	11	1.1
Number of Samples	2532-2998 (avg. 2617)	56	1150
Reference	112	39	113

is supported by the fact that the "Superfund" sites were of concern as potentially contaminated areas, while the New York State samples were from public water supply wells. It is quite difficult to determine from the reported data whether analytical bias entered into these data sets from sampling or analytical procedures. This is an area which deserves careful attention in an overall ground-water monitoring effort.

Polyethylene and polypropylene are clearly superior plastic materials for sampling applications in situations where Teflon® is not cost-effective. Teflon® is the tubing material of choice in monitoring for low-level organic compounds in complex, chemically aggressive environments. Silicone rubber tubing for moving components of sampling devices represents a special case where alternate choices of material may not be feasible. The material is available in several grades which have widely varying compositions and additives. Metallic contamination from certain laboratory grades of silicone rubber tubing can be quite serious at the ppb level. Fe and Zn concentrations 2-5 times those of control samples are not uncommon even after short contact times (146). Medical-grade silicone rubber tubing is relatively free of unreacted organic initiators (peroxides) or zinc and is a reasonable alternative to other tubing formulations. Together with the potential bias introduced by the suction mechanism of peristaltic pumps, the need for silicone rubber tubing makes it a poor choice of sampler for detailed organic analytical schemes. The use of other elastomeric materials, such as natural rubber, latex, neoprene. or chloroprene, is not recommended for transfer lines or surfaces that contact ground-water samples.

There is little information available on the performance of flexible materials in ground-water applications. From the available observations, Teflon®, polypropylene, and linear polyethylene may be expected to outperform plasticized PVC, since they have superior chemical resistance over a range of environments and are less likely to cause contamination or bias problems. Microbial transformations of plastics' additives introduces another dimension to the problem posed by materials with high concentrations of additives. There are a number of reports on the microbial colonization of flexible PVC and the degradation of plasticizers from the polymer matrix (147).

The closest evidence to actual field testing of flexible materials comes from the testing of landfill liners by exposure to municipal leachate (148) or actual waste streams (149). These observations were obtained on plasticized PVC and 11 other landfill liner materials. A major conclusion of the work confirms the overall superior performance of plasticized PVC over most elastomers or chlorinated polyolefinic materials.

Storage containers

The choice of materials for sample storage containers for monitoring programs has been made by the USEPA after 15-20 years of development by environmental scientists all over the world. The choice of container materials is dictated by the group of analytes of interest and the prescribed preservation techniques. Inorganic constituents are determined in samples stored in high density linear polyethylene bottles, with the exception of ammonia, sulfide, or ferrous iron. These species demand oxygen-impermeable glass containers and short storage times prior to analysis. Organic chemical constituents, including priority pollutant classes, TOC, and COD, are required to be stored in glass bottles with Teflon®-lined screw caps.

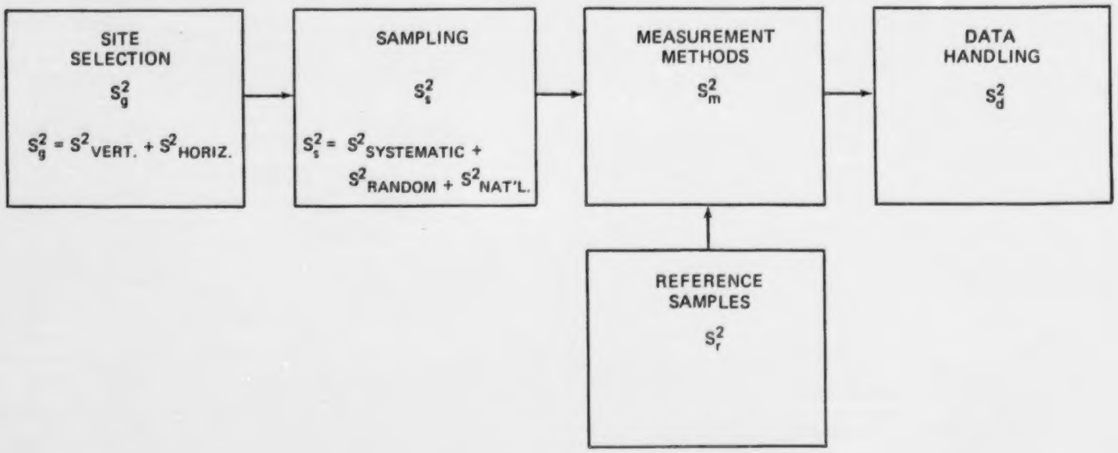
Details on specific preservation procedures, sample volumes, and limits on sample storage times are contained in several reference works (150,151). It is reasonable to expect that preservation procedures for organic surrogate parameters such as BOD, COD, and TOC are minimal steps to preserve samples for specific organic compounds at the ppb level.

Sources of Error in Monitoring Efforts

In Figure 7-1, sources of error contributing to the overall variance (square of the standard deviation from the mean) of ground-water monitoring program data are schematically depicted. Site selection, sampling, and the analytical problems of measurement, reference samples and data handling are the principal contributing factors. The overall variance (S^2) associated with each factor must be known and minimized in order to permit reliable comparisons of related data sets. The relative magnitude of analytical error and errors due to site selection or sampling will determine whether systematic problems in network design, genuine trends, or significant concentration differences can be observed in related samples.

Errors may be classed as systematic or random. Simply stated, random errors enter into overall determinations by handling or human failures and contribute to the lack of precision in a methodology. Systematic errors are the inherent sources of bias or inaccuracy in an overall determination which may consistently prevent the reporting of an accurate result. In ground-water monitoring, the overall determination of a chemical constituent in a sample from a particular well includes flushing of standing water to permit collection of a representative sample; sample collection; handling and storage; and execution of the appropriate analytical laboratory method.

For example, if a particular chemical constituent can be determined analytically with a precision of ±20% relative standard deviation, then errors arising from site selection or sampling must be less than ±20% to permit reliable evaluation of statistically significant differences in related samples. If, on the other hand, systematic sampling



Thus the overall variance = $S^2 = S_g^2 + S_s^2 + S_m^2 + S_r^2 + S_d^2$

Figure 7-1. Sources of error involved in ground-water monitoring programs contributing to total variance

error (biased accuracy) caused by the introduction or loss of this constituent from a particular sampling results in worsened overall precision, there is a danger of reporting a false positive or no trend when, in fact, an unbiased series of samples would show the opposite to be true. This type of problem may go undetected and has been discussed by several authors (102,152,153, 154).

To ensure quality and inter-comparability of ground-water monitoring data, one must seek to eliminate the systematic sources of error (contamination, loss, or introduction of an interfering constituent) and minimize the random errors due to handling or human intervention. Systematic sampling errors could arise from poor drilling techniques, the use of persistent drilling fluids, improper well development, poor choice of well casing, or inappropriate sample handling materials for the hydrochemical environment. Sample collection mechanisms and techniques also can significantly bias analytical results.

It is obvious that the choice of materials is a controllable source of systematic error. Whether or not *materials'* selection can adversely affect the quality of the analytical data will depend on the concentration range for the specific chemical constituents of interest, the magnitude of analyte loss, contamination or interference contributed by the material, and the performance data for the respective analytical methods.

Comparison of analytical method performance with materials' related errror

In order to best present the background information on various materials which will aid in making an appropriate selection, we have chosen two degrees of analytical detail for hypothetical monitoring programs. The simplest program is patterned after minimum RCRA compliance involving TOC (total organic carbon), TOX (total organic halogen), pH, and Ω^{-1} (specific conductance) determinations. The more detailed approach will involve a complete priority pollutant scan on the ground-water samples. The reported precision, accuracy, and routine detection limits for the analytical determinations will be discussed.

A minimal monitoring program may include the determination of selected indicator variables such as pH or conductance and organic surrogate parameters (TOC or TOX) to detect changes in the chemical quality of ground water. The introduction of acidic or basic contaminants in excess of natural buffer capacity would be indicated by pH changes, and these, as well as other inorganic substances, may cause a change in ionic composition which would show up in the solution conductivity. Increases in TOC and TOX may be expected to signal the introduction of organic compounds or halogenated organics. The significance of changes in these parameters over time is judged by statistical comparison of results from upgradient and downgradient wells. One may argue that if both wells were constructed identically, the effects of materials on the analytical results would be minimal. This may be true when the hydrochemical environments at each well site are identical. However, it is precisely when there is a chemical difference between the subsurface zones as a result of a release that the need is greatest for reliable signals from high-quality (unbiased) analytical data. Table 7-10 contains performance data on the analytical determinations of TOC, TOX, pH, and Ω^{-1}. The table includes precision data for repetitive determinations at various values of these parameters and corresponding accuracy information. Precision is reported as the relative standard deviation (r.s.d.) expressed as a percentage of the mean value. Accuracy

Table 7-10. Analytical Performance Data for Selected Water Quality Parameters

Parameter (method)	*Type of determination* *	*Value*	*Precision (relative standard deviation) %*	*Accuracy (as bias) %*	*Practical detection limit* $(mg \cdot L^{-1})$	*Reference*
TOC (combustion-infrared)	I	$4.9\ mg \cdot C \cdot L^{-1}$	80	+15.27	0.10	150
		107 "	7.8	+1.01		
	S	$15.8\ mg \cdot C \cdot L^{-1}$	14.0	−11.4		155
		36.1 "	17.9	−21.9		
TOX (C-trap, pyrolysis, conductivity)	S	$0.09\ mg \cdot C1^{-}_{org} \cdot L^{-1}$	6.0	+7.0	0.01	156
pH (electrometric)	I	3.5 (pH units)	3.0	−0.29	NA	150
		7.1	2.8	+1.01		
		8.0	1.6	−0.12		
	S	7.7	1.3	–		150
Ω-1 (conductivity bridge)	I	100 (micro Siemens)	7.6	−2.02	NA	150
		808	8.2	−3.63		
		1640	6.5	−4.54		
	S	536	1.1	–		150

* I = Interlaboratory Comparison; S = Single Laboratory Results

is reported as bias or the difference of the analytically determined value from the "true" or assigned value. Accuracy is the critical value to examine for the effect of systematic errors. In an actual monitoring program, one would be careful to note a significant decrease in precision (increased r.s.d.) for repeated determinations on natural samples, since the "true" or assigned value is not known. The goal, of course, is to get *representative* samples.

From Table 7-10 it is clear that the more involved procedures for the surrogate parameters (TOC and TOX) involve considerably larger relative standard deviations and more variable values of analytical bias than do the direct instrumental methods for pH and Ω^{-1}. To some extent this is due to differences in laboratory conditions and operator consistency, and in the overall efficiencies of the methods for standard compounds. For high-quality data, sampling or site selection bias should be less than the values for analytical bias. Therefore, one should weigh the potential for materials' effects in situations where they may contribute bias approaching that practically attainable in the analytical method. For example, consider the use of plastic storage bottles which can contribute 2-3 $mg \cdot C \cdot L^{-1}$ consistently to TOC samples. At TOC levels below 10-15 $mg \cdot C \cdot L^{-1}$, this level of leached material would bias the determination by more than 20 percent which would exceed the analytical bias. A grossly inaccurate analytical result would be observed, so this material is clearly inappropriate for the application. A similar treatment would extend to the other parameters in Table 7-10.

The overall determinations of the surrogate parameters (TOC, TOX) or solution properties such as pH and conductance are probably not very sensitive to materials' effects, since they measure classes of compounds or electrolyte properties. Gross errors in this type of program would probably result from improper construction or sampling techniques, particularly inadequate well flushing prior to sampling.

In a more detailed analytical data collection effort, the effects of materials may be much more critical, since low levels of degradation or corrosion products and leachables could directly bias the determination of specific chemical species at concentration levels well above detection or quantification limits. Sampling bias, apart from material-related errors, remains a large gap in our understanding of overall inaccuracies in the data. In this respect, each case must be carefully considered with regard to the relative magnitudes of contributing errors for the contaminants of interest.

Tables 7-11 and 7-12 contain analytical method performance data for inorganic and organic chemical constituents which might be included in a comprehensive interpretive monitoring program. The performance data on these analytical methods reflect the optimum condition of good laboratory practice and high-quality reagent water. Table 7-11 details performance data for inorganic chemical parameters which provide an indication of water quality and the presence of inorganic contamination. The precision and accuracy values are expressed as they were in Table 7-10. The tabulated values indicate that routine analytical reproducibility is generally better than 20 percent and that the mean may be expected to be within about 10 percent of the "true" value. Detection limits for the anionic constituents are in the ppm range, while those for the metallic elements are in the low ppb range. The same overall accuracy and precision ranges apply to the priority pollutant organic compounds in Table 7-12. Modern analytical instrumentation enables the precise determination of many metallic elements and organic compounds on a routine basis. Although accuracy varies somewhat for compounds such as benzidine and the phthalate esters, a conscientious laboratory staff can adjust raw analytical results for actual recoveries through the use of suitable

Table 7-11. Analytical Performance Data for Selected Inorganic Chemical Constituents

Parameter (method)	*Type of determination**	*Precision (relative standard deviation) %*	*Accuracy (as bias) %*	*Practical detection limit ($mg \cdot L^{-1}$)*	*Reference*
CL^-	I	9.1	2.16	1.0	150
(titrimetry)		3.1	-0.61	1.0	
	S	2.9	–	–	
$SO_4^=$	I	19.3	−8.26	1.0	150
(turbidimetry)		5.9	−1.70	1.0	
Alkalinity	I	15.9	+10.61	–	150
(titrimetry)		4.5	−7.42	–	
NO_3^-	I	43.7	+8.30	0.1	150
(colorimetry)		17.3	+2.82	0.1	
Major Cations: Ca, Mg, Na, and K (AAS)†	S	4.4	±2	0.01	150
Trace Metals: Fe, Mn (AAS)†	I	27.8	±3	0.03	150
Pollutant Metals: Cu, Cd, Pb, Ni, Zn	S	4.6	±6	0.01	155,157
(AAS) ††	S	5.2	±7	0.01	

*I = Interlaboratory Comparison; S = Single Laboratory Results

(AAS)† = Atomic Absorption Spectrometry–Direct Aspiration/Flame

(AAS)†† = Atomic Absorption Spectrometry–Graphite Furnace/Flameless

Table 7-12. Analytical Performance Data* for Selected Organic Chemical Constituents

Compounds	*Precision (relative standard deviation) %*	*Accuracy (as bias) %*	*Practical detection limit (ppb)*	*Reference*
Volatiles				
benzene	12.0	29	10**	143,156,157
chlorobenzene	13.1	−6	10	
1,1-dichloroethane	19.1	5	10	
1,1,2-trichloroethane	12.8	−5	10	
trichloroethylene	14.0	6	10	
tetrachloroethylene	13.0	−20	10	
chloroform	17.5	10	10	
ethyl benzene	12.5	−7	10	
toluene	12.6	−4	10	
o-xylene	7.0	−5	10	
Base-Neutrals				
anthracene	20.0	−7	10	143,156,157
benzidine	22.0	−66	>10**	
benzo (A) pyrene	22.0	11	10	
bis (2-ethylhexyl) phthalate	18.0	20	10**	
2-chloronaphthalene	20.0	−14	10	
chrysene	33.0	−16	10	
1,2-dichlorobenzene	13.5	−9	10	
hexachlorobenzene	42.0	50	10	
nitrobenzene	21.0	38	10	
1,2,4 trichlorobenzene	22.0	−26	10	
4-chlorophenyl phenyl ether	5.0	−2	10	
*Acidics***				
o-chlorophenol	22.0	10	25	143,156,157
2-nitrophenol	20.0	5	25	
2,4-dichlorophenol	20.0	5	25	
phenol	19.0	−39	25	
pentachlorophenol	31.0	14	25	
4-nitrophenol	20.0	−5	25	
2,4,6-trichlorophenol	26.0	10	25	
*Pesticides***				
aldrin	8.0	−16	10	143,156,157
4,4′ DDT	29.0	−23	10	
dieldrin	2.5	−3	10	
endrin	11.0	−6	10	
heptachlor	11.0	−41	10	
chlordane	5.0	−20	10	

*The data represent average minimum levels of precision and accuracy obtainable by the referenced laboratories using 600 series Priority Pollutant Methods. Detection limits are those estimated levels routinely achieved by several laboratories for aqueous standards in each class. These values will vary considerably depending on the analyst and whether GC/MS, GC^2/MS, or chromatographic methods with selective detectors are used.

**Interlaboratory values varied over an extremely wide range (greater than one order of magnitude), particularly for methods 624 and 625.

standards carried through the procedure. The laboratory staff cannot be expected to account for sampling or materials-related errors in the analytical results.

For the trace contaminants in Tables 7-11 and 7-12 determined at the 10 ppb level, one may expect that the corrected analytical results will be within 20 percent of the actual value in the absence of bias or unknown interferences. It is the responsibility of the monitoring program director to inform the lab of any known interferences as well as sampling procedures and materials' contacted which may bias the analysis of ground-water samples. For example, it has been shown by several groups that solvent cements used in the construction of PVC well casing and bailers contain chemical constituents which directly interfere with the chromatography of several priority pollutants (41,79, 116). Such interferences may persist for many months, even after proper development of solvent-cemented PVC monitoring wells. It may be possible to assess analytical problems by saving a sample of the PVC primer or solvent cement for complete analysis. However, the composition of these products has been shown to vary significantly from that noted on the label (41).

There are many other sampling and materials-related problems which can bias the analytical data from monitoring programs. Several decades of study on the effects of such artifacts have resulted in significant improvement in the quality of chemical data. This process has taken place in fields as diverse as oceanography (117,158) and lunar geochemistry (159), where the effects of "conventional" sampling gear or an inadvertant fingerprint have led to substantial confusion in the scientific literature. Ground-water monitoring programs can benefit from this body of experience, even though the aims of such efforts are more practical.

SECTION 8
COST CONSIDERATIONS

Once the goals of a ground-water monitoring program have been identified, an estimate must be made of the costs that will be incurred in all the various tasks of data collection. Preliminary screening of existing data and hydrologic and geophysical surveys are valuable planning tools which provide estimates of the type, extent, and costs of data collection. Professional consultation can supplement this planning by identifying potential options for altering network design in the event of specific contingencies. As a rule, the degree of detailed information to be collected is roughly proportional to the cost of the effort to obtain it. Both the minimum quantity and quality of data, as well as the maximum, must be incorporated into the monitoring plan. Since there are many unknowns involved in ground-water investigations, the maximum cost/benefit condition may be achieved by designing the initial plan so that minimum information needs will be met and at least part of the network design will serve future needs. Careful consideration of data reporting and standards for high-quality data are available to aid this effort (160).

Water chemistry data collection entails the siting and construction of wells and sampling points followed by the collection, analysis and evaluation of the analytical data. The analytes of interest, necessary sensitivity, precision and accuracy at specified limits of quantitation must be identified in the planning stages. From this point, the particulars of materials' selection, sampling protocol development and prospective interpretive techniques can be planned to insure that high-quality information is collected in a cost-effective manner.

The preceding chapter dealt with the selection of appropriate material for a range of ground-water conditions. Also, sources of potential bias or inaccuracy which can result from the use of inappropriate materials in contact with water samples were identified. The choice of well casing (or sampling device) materials is a key element in planning a ground-water monitoring effort for two reasons. First, all of the water samples pass through this point. Secondly, once the initial sampling points of a network are constructed, it will require significant cost and effort to replace them should their emplacement or interactions with the subsurface render them useless. An additional caution in material selection is that bias or inaccuracy may be detected too late to salvage even the minimum information required for program success. All of the other materials which contact the samples can be independently evaluated for potential bias and replaced if necessary while the program is in motion. Fortunately, the case for choosing appropriate well casing materials can be made on a reasonable cost/benefit basis.

The following discussion details the relative costs of essential elements of general ground-water monitoring efforts, including well drilling and construction, sampling, and analysis. Relative costs are presented for four suitable combinations of well construction materials over a range of analytical complexity. It is presented as an example of potential planning scenarios for a successful, cost-effective monitoring program. A very detailed consideration of the costs involved in monitoring efforts has been developed by Everett et al. (37).

Description of an Example Monitoring Effort

For purposes of discussion, assume that a network of one upgradient and three downgradient, 2-inch, 50-foot wells is to be constructed at a waste disposal site. The wells are to be completed at 48-foot depths with 2 feet of screen and approximately 2 feet of casing above ground surface. The screened interval was chosen from the results of a hydrogeologic and geophysical survey. Contract drilling/well construction services will be used. Sampling is to be done by salaried personnel, and the purchase of some equipment for sample collection and field determinations will be necessary. Since very little chemical information is available on the wastes involved, the site, or conditions, a range of analytical schemes must be considered. The principal questions in the mind of the monitoring network design staff are: What are the background chemical conditions present in ground water upgradient from the site? How do we distinguish background chemistry from chemical species which may be contributed by the waste? How do we choose well construction materials so that we can obtain representative samples of ground water if both inorganic and organic contaminants may be found? The decision is made that the initial network design and installation of sampling points will be operated for at least 5 years unless the results of the first year's sampling indicate that additional wells or an expansion of the design is necessary. The cost-effective choice of well casing materials needs to be made in order to insure the quality of the analytical information and to build a degree of flexibility into the 5-year program.

Well Installation and Sampling Costs

Consideration of the optimum requirements for reliable techniques and materials for well construction or sampling presented in the preceding sections limits the spectrum of drilling techniques and materials' selection. Specific choices among the possible combinations are likely to be very situation-dependent. Therefore, the cost detail for key elements of monitoring efforts will be somewhat general.

Three types of well casing/screen are to be considered: threaded rigid PVC (unplasticized), 304 stainless steel (SS), and Teflon®. The costs involved in using paired PVC/SS wells are developed to enable comparison with Teflon®. Pairs of PVC/SS wells appear to be a reasonable alternative when a range of inorganic and organic contaminants are of interest under conditions where either PVC or SS may be attacked or otherwise introduce bias into subsequent analytical determinations. These three material combinations are recommended for well casing materials selection in planning a monitoring effort.

Table 8-1 contains a breakdown of approximate well construction and sampling costs for the first year's operation of a monitoring effort. Drilling costs were estimated in 1983 dollars for the mobilization and operation of a hollow-stem-auger drill rig and for the installation of four wells. The costs for well construction materials were developed for manufactured casings/screens currently available from commercial

Table 8-1. Cost Estimates for Drilling, Well-Construction, and Sampling

(In 1983 dollars)

Drilling				*1st Year*
Mobilization (within 150 miles)				$ 700
Hourly Fee				3000
(4 50-ft wells with 2" casing at 10 $\text{ft}\cdot\text{hr}^{-1}$ plus formation sampling)			Subtotal	$ 3700
Well Construction Materials	*PVC*	*SS*	*PVC/SS*	*Teflon®*
Well casings and screen (2 ft)	700	2000	7900*	8700
Fittings, Well Protectors**	640	640	640	640
Cement, Sand, Bentonite	460	460	460	460
Subtotal	$1800	3100	9000	9800
*Sampling****				
Quarterly (10 $\text{man-days}\cdot\text{yr}^{-1}$; at $\$15{,}000\cdot\text{yr}^{-1}$)				
Staff				$ 600
Supplies				300
Equipment (pH and conductivity meter, electrodes, samplers and filtration apparatus)				3450
			Subtotal	$4350
First year costs for drilling, well construction materials and sampling	**PVC** **$9850**	**SS** **11,150**	**PVC/SS** **17,050**	**Teflon®** **17,850**

*includes cost of extra drilling necessary for PVC/SS pairs
**optional for SS wells
***field determinations of pH, conductance, and alkalinity are assumed to be included in sampling operations

suppliers. The added cost involved in drilling pairs of wells for the PVC/SS option was included in the materials cost for purposes of comparison. Sampling costs were developed by including staff, supplies and equipment outlays for the first year. This procedure lumps together capital, personnel, and operating cost categories for purposes of comparison. Details of financing arrangements and calculation of the actual cost of a monitoring program must be made by the individuals involved on a case-specific basis. It is clear from the data in the table that the first-year well construction and sampling costs for a PVC well network versus one of stainless steel differ by less than 15 percent. For a program initially aimed at assessing background chemical conditions, the added cost of installing stainless steel wells may be warranted to provide a degree of flexibility in future operation should organic contaminants later be encountered. The paired PVC/SS and Teflon® monitoring arrays are significantly more expensive to construct and sample but are cost-effective choices in chemically aggressive subsurface situations.

A graphical comparison of the capital costs for drilling and well construction as a function of depth is shown in Figure 8-1. The figure projects a linear increase in costs correlated with the depth of monitoring interests and demonstrates the similarity in capital costs between the PVC, SS and the PVC/SS or Teflon® options. An important note here is that considerable cost savings may accrue from casing the upper zones of the well bore with a less expensive material and using a more appropriate material below static water levels.

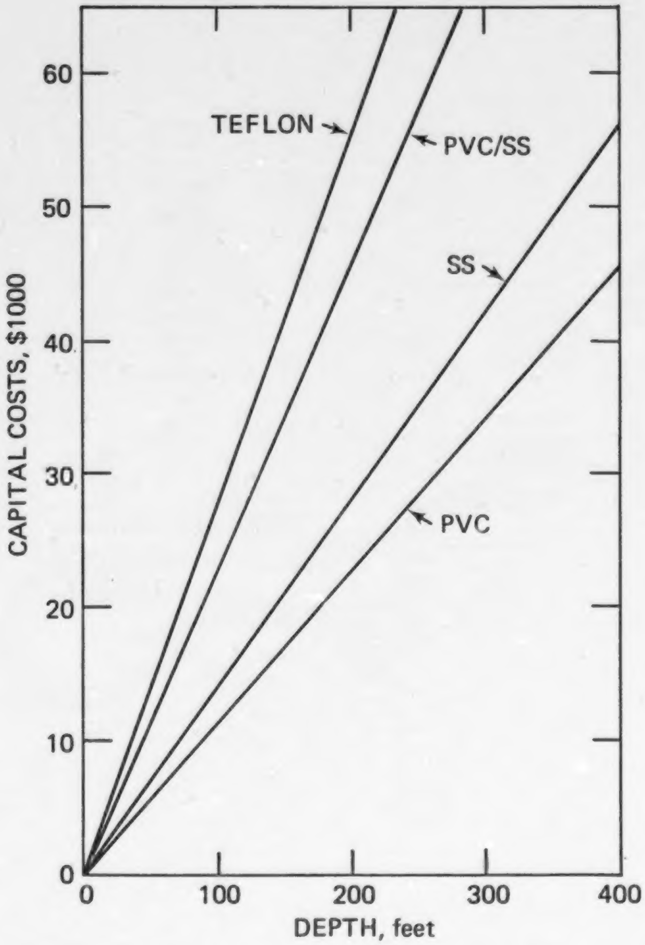


Figure 8-1. Capital costs for drilling and well construction of four point array

Analytical Costs

The minimum degree of analytical detail necessary to adequately meet the needs of ground-water monitoring programs varies significantly according to program goals. In regulatory monitoring efforts, the prescribed parameters may be mandated and the successful performance of the monitoring effort may be little more than an exercise. There are pitfalls in this minimal approach. For example, natural variations in ground-water chemistry may not be evident from quarterly determinations of "contaminant-indicator" parameters (e.g., RCRA analytical parameters, pH, specific conductance, Total Organic Carbon, and Total Organic Halogen). If natural variability in the background electrolyte chemistry is high, it may prove quite difficult to distinguish natural versus contaminant-release fluctuations. A minimal interpretive analytical scheme should include indicator parameters as well as a total-dissolved-mineral analysis in order to provide a basis for future work as well as checks on sample handling and analytical procedures. This approach also enables close analytical quality control via mass and charge balances for the evaluation of "representative sample" information. Further, more detailed interpretive monitoring schemes eventually may be called for at the site of interest. Well construction techniques and materials should be chosen to permit expansion of the analytical scheme, as well as monitoring network goals, should the need arise. After background conditions have been established in the early stages, the goals can be extended and specific parameters of interest can be added to serve the more demanding needs of detailed interpretation. Well-conceived network planning, design, and operation will support the detailed information needs which may be encountered in the future.

In Table 8-2, four sample analytical schemes and corresponding derived parameters are listed. Average prices have been included from the price quotes of three high-volume analytical laboratories based on a minimum of ten samples (including replicate, field blanks, and field standards) per submission. One can see that as the number of individual analytes is increased, the cost per sample increases proportionately for detailed inorganic and organic analysis.

After the degree of analytical detail appropriate for the program has been chosen, a sampling frequency must be determined. Also, the number of replicate samples must be decided upon in order to provide the necessary precision for evaluation procedures. The sample monitoring program has been designed for quarterly sampling frequency using the four analytical schemes shown in Table 8-2. At least duplicate

Table 8-2. Description of Analytes and Costs for Four Analytical Schemes for Ground-Water Samples

	Total	*Dissolved (field-filtered and preserved)*	*Cost per sample*†
1. *Minimal Detective*			
pH, Ω^{-1}, TOC, TOX	*		75.00
2. *Minimal Interpretive*			175.00
pH, Ω^{-1}, TOC, TOX	*		
Alk, Cl^-, NO_3^-, $SO_4^=$, $PO_4^\equiv$, SiO_2		*	
Na^+, K^+, Ca^{++}, Mg^{++}, Fe, Mn		*	
3. *Inorganic Interpretive*			410.00
pH, Ω^{-1}, TOC, TOX	*		
Alk, Cl^-, NO_3^-, $SO_4^=$, $PO_4^\equiv$, SiO_2, B		*	
Na^+, K^+, Ca^{++}, Mg^{++}, Fe, Mn		*	
Fe(II), Zn, Cd, Cu, Pb, Cr, Ni	*	*	
Ag, Hg, As, Sb, Se, Be, Tl		*	
4. *Detailed Interpretive*			1400.00
All of the above (3) PLUS			
Volatiles (Method 624)	*		
Base-Neutrals (Method 625)	*		
Acidics (Method 625)	*		
Pesticides (Method 608)	*		

†Costs determined in 1983 U.S. dollars from the average of three high-volume analytical services using EPA approved methodology.

A minimum of ten samples per submission is assumed.

samples of ground water from each well are to be collected, or one may elect to concentrate more replicates on the upgradient and one particular downgradient well.

Five-year total costs are detailed in Table 8-3 for several combinations of analytical schemes and sample replication. The number of samples per year includes at least one field blank and field standards per sampling date at the stated level of replication. The 5-year totals for analytical costs have been calculated at a 5 percent annual increase in the cost of these services. In comparison with the first-year drilling, well construction and sampling costs presented in Table 8-1, it is evident that analytical costs (even for a minimal monitoring effort) make up a large share of total project costs. Of particular note is the fact that in a detailed interpretive network (3A, 3B, 4A, 4B), the difference between choosing PVC over stainless steel well casing material (which is less likely to introduce bias into the analytical data) results in a cost "savings" of $1300. A comparison of reanalysis costs with apparent savings by the choice of a cheaper material (PVC) over stainless steel are shown in Table 8-4. One can readily see that the expected "savings" realized from the use of an inappropriate, cheaper material are actually penalties.

Table 8-3. Analytical Cost Detail*

Analytical scheme	*Samples· yr^{-1}*	*Cost ($)* *1 Year*	 *5 Years***
1. Minimal Detective (4 replicates of each sample)	80	4,800	26,523
2. Minimal Interpretive (Duplicates of each sample)	48	8,400	46,415
3. A – Inorganic Interpretive (4 replicates in lst year; duplicates in years 2-5)	80/48	32,800	121,864
3. B – Inorganic Interpretive (Duplicates of each sample)	48	19,680	108,744
4. A – Detailed Interpretive (4 replicates in 1st year; duplicates in years 2-5)	80/48	112,000	416,122
4. B – Detailed Interpretive (Duplicates of each sample)	48	67,200	371,322

*Quarterly sampling of 4 wells; unless otherwise specified, 4 replicates plus field blanks and field standards in duplicate for each analytical workup. Field determinations: pH, Ω^{-1} and alkanlinity included in sampling costs.

**Calculated at a 5% annual increase in cost.

Table 8-4. Comparison of Reanalysis Cost with Cost "Savings" on Materials

Analytical scheme	*Single sample reanalysis cost ($)*	*Materials† "savings" ($)*	*Actual "savings" ($)*
1	450	1300	850
2	1050	1300	250
3A	2460	1300	–1160
3B	1640	1300	–340
4A	8400	1300	–7100
4B	5600	1300	–4300

†Difference between PVC versus stainless steel well construction materials

Project Cost Comparisons for Selected Materials' Combinations for Networks of Varying Analytical Detail

The example monitoring network has been developed as a general guide for planning network design. Though the emphasis has been on well casing materials, the methodology applies as well to the choice of materials for sampling gear or tubing. To put the costs of total project implementation and well casing material in perspective, it is a relatively simple matter to repeat the process for a specific case to complete the cost/benefit analysis.

In Table 8-5, the approximate total project costs for the sample analytical schemes and various well casing materials are presented. It is evident that the incremental increases for more ideal (and costly) materials is far less than the increases incurred in satisfying more involved analytical needs. On the basis of initial material costs, the most expensive materials options, paired PVC/SS and Teflon®, make up a small percentage of total project costs. One must carefully weigh the value of the information needed versus the "insurance" value of making appropriate choices of materials which may contact the samples. For long term five-year project operations, stainless steel clearly is the material of choice for minimal analytical schemes.

The selection of materials for pumps and tubing are important to both the reliability and the cost/benefit considerations of ground-water monitoring programs. They are somewhat less critical than materials for well construction since there are few significant additional costs (e.g., drilling, mobilization, etc.) that must be included as well, except in the case of dedicated samplers. The cost comparison can be made in a similar fashion to that for well drilling and construction.

Table 8-5. Total Project Costs for Monitoring Programs

($1.0K 1983 dollars rounded to nearest $0.5K)
including the Percentage of Materials Costs

	1st Year				*5 Years†*			
Materials	*PVC*	*SS*	*PVC/SS*	*Teflon®*	*PVC*	*SS*	*PVC/SS*	*Teflon®*
Analytical Scheme								
1. Minimal Detective	14.5	16.0	22.0	22.5	42.0	43.5	51.5	50.5
% Increase over PVC		10	38	55		4	23	20
2. Minimal Interpretive	18.0	19.5	25.5	26.0	62.0	63.0	73.0	70.0
% Increase over PVC		8	42	44		2	18	13
3A. Inorganic Interpretive	42.5	44.0	50.0	50.5	137.5	139.0	147.0	146.0
% Increase over PVC		3	17	18		1	7	6
3B. Inorganic Interpretive	30.0	31.0	37.0	37.5	124.0	125.0	134.0	132.5
% Increase over PVC		3	23	25		1	8	7
4A. Detailed Interpretive	122.0	123.0	129.0	130.0	431.5	433.0	441.0	440.0
% Increase over SS	NR		5	6	NR	<1	2	2
4B. Detailed Interpretive	77.0	78.0	84.0	85.0	387.0	388.0	396	395.0
% Increase over SS	NR		8	9	NR	<1	2	2

†5 year project costs calculated using yearly totals, including: 1% annual increases per year for maintenance on well installations and 5% annual increases per year for supplies, sampling staff time and analytical services. (PVC/SS installations require twice the maintenance effort and therefore exceed all Teflon® costs after 5 years.)

NR — Material is not recommended for use with a detailed organic analytical scheme due to the likelihood of analytical bias and imprecision.

Tailoring the Monitoring Well and Sampling Apparatus to the Anticipated Analytical Scheme

The successful planning of a monitoring program demands the consideration of several factors: the ultimate goal of the monitoring program; the hydrologic conditions of the site to be monitored; the sources of pollution and their chemical nature; the quality of the ground water to be protected; the levels at which selected indicator and specific monitoring parameters are to be analyzed; and appropriate cost-effective choices of materials, drilling or sampling techniques.

Given these factors, preliminary decisions can be made concerning the location, depth, physical features, and materials selection for the monitoring wells. Appropriate drilling and well development techniques also must be selected. It is important to maintain flexibility in this preliminary planning stage because the initial monitoring plan may require revision as new information is collected during well construction. Preliminary planning must be undertaken after consideration of the complexity of the analytical scheme.

The objective in siting a monitoring well is to place the screened interval in the predicted flow path of contaminant migration from the monitored site. Optimum placement should allow for early detection of contamination to prevent a crisis situation caused by the undetected migration of pollutants. Well construction materials should be selected to minimize bias and interference with anticipated pollutants at the specified levels of analysis. Careful attention should be given to possible expansion of the original information needs of the monitoring effort.

The selection of sampling apparatus also should be based on the proposed analytes of interest and planned (as well as achievable) levels of detection. Sampling devices should be selected so that neither their component materials nor their pumping operation will significantly alter solution chemistry.

In the case of detective monitoring, consideration should be given to the use of the monitoring wells and sampling apparatus in a more rigorous interpretive monitoring program. Upgrading wells and sampling devices in the early phases of monitoring may save considerable time and expense later. Trying to save money by compromising on materials quality or suitability in detective monitoring may eventually increase program cost by causing reanalysis or triggering unwarranted interpretive monitoring. The choice of appropriate robust materials and proven methods can provide significant long-term benefits to a well-conceived program.

In summary, each monitoring program must be approached on the basis of its own information needs and conditions. There are no standard monitoring approaches that prove satisfactory for all sites. The multiple goals of monitoring projects, the heterogeneity of geologic materials, temporal and spatial variability in chemistry and hydrology, and the wide variety of chemicals to be monitored provide an unlimited number of unique conditions that call for different approaches to monitoring. All of these factors must be examined to determine the impact they may have on the reliability of the analytical data as well as the long-term costs and benefits involved in obtaining this information.

SECTION 9
CONCLUSIONS

Ground-water monitoring is an important part of a reasoned resource management and protection strategy. Monitoring programs include the modeling, planning, analysis and interpretation of information on the subsurface environment of ground water. These programs can be expensive as well as time consuming. However, with careful planning of field efforts, the yield of high quality information will prove to be invaluable to our understanding of the dynamics of ground-water systems.

Critical considerations for the design of monitoring networks are the selection of drilling and sampling techniques in addition to the choice of materials which will contact groundwater samples. With the knowledge of the principal chemical constituents of interest, local hydrogeology, and an appreciation of subsurface geochemistry, appropriate selections of materials, drilling, and sampling techniques can be made. Whenever possible, physical disturbance and the amount of foreign material introduced into the subsurface should be minimized.

The choices of drilling methods and materials for both well casing and sampling apparatus are very important decisions to be made in every type of ground-water monitoring program. Details of network construction can introduce significant bias into monitoring data which frequently may be corrected only by repeating the process of well siting, installation, completion, and development. This can be quite costly in time, effort, money, and loss of information. Undue expense is avoidable if planning decisions are made cautiously with an eye to the future.

Sampling techniques similarly should be tailored to the information needs and goals of the monitoring efforts. If appropriate network design decisions are made, the effect of sampling errors can be corrected before major decisions on expansion of the monitoring goals are necessary.

The expanding scientific literature on subsurface phenomena and effective ground-water monitoring techniques should be read and evaluated on a continuing basis. This information alone will supplement published guidelines and suggestions for application to specific monitoring efforts in the future.

SECTION 10
RECOMMENDATIONS

General Recommendations

The Agency should focus its aid and technical assistance to state ground-water management and protection efforts so as to encourage a degree of uniformity and consistency in monitoring efforts. A central element of federal policy should include a mechanism for the retrieval and interpretation of monitoring information which includes detailed site-specific data on network design, construction, and operation to minimize the continued use of unreliable techniques or incompatible materials which result in useless data collection. Of necessity, this must be conducted to protect source confidentiality in some instances, but this requirement should not prove to be an impediment to effective technology transfer.

Similarly, the claims of manufacturers or ground-water professionals concerning the integrity of materials, the reliability of specific designs or techniques, and the performance of sampling equipment should be very carefully evaluated on a case by case basis. The concerted attention of design, technical, and analytical staff should be trained on each aspect of a ground-water monitoring effort before the implementation of the network.

Specific Recommendations

Non-contaminating drilling methods are available to provide access holes to the geologic formation of interest which need not be overly expensive or expose workers to undue hazard even in badly contaminated situations. Well casings and screens should be selected with the understanding that analytical requirements demand a durable, stable sampling point which can be relied upon to maintain the integrity of the *in-situ* ground-water condition. Well casing and screen materials in decreasing order of preference for most monitoring situations are:

Teflon®, stainless steel, and rigid threaded PVC

Commercially manufactured casing products are recommended over home-made varieties. The choice of inappropriate, less expensive well casing/screen materials is rarely cost-effective even in minimal monitoring efforts with limited analytical detail. Future contingencies and the cost of reanalysis can convert apparent "savings" into real costs with a corresponding penalty in lost time, effort, and information. The convenience of using PVC well casing or screens must be carefully considered in this regard since the potential for biased analytical data clearly exists in detailed analytical schemes.

The methods and materials involved in ground-water sampling are equally critical to the collection of high quality monitoring information. Overreliance on simple, traditional collection mechanisms (e.g., bailing) entails a serious potential for the continued collection of unreliable, poor data particularly where the analysis of volatile, pH-sensitive, or reduced chemical constituents is of interest. Integral sampling methods which minimize turbulence, atmospheric content, gas exchange, and depressurization are preferable for these applications. Materials which contact water samples during collection are no less critical than storage vessels. Recommended materials for pump parts, tubing, and associated apparatus in decreasing order of preference are:

> Teflon®, stainless steel, polypropylene, polyethylene, linear polyethylene, Viton®, conventional polyethylene, PVC

Though other materials appear promising from the standpoint of structural integrity and chemical resistance, there are very few hard data on which to recommend their use in ground-water monitoring.

Ground-water monitoring is more complex and challenging than the collection of reliable data in natural surface waters. The lessons of past monitoring efforts clearly demonstrate the need for multi-disciplinary inputs to planning ground-water investigations. The input of both chemical professionals and laboratory personnel is essential to a successful program.

The wise monitoring program director should attempt to consider carefully all existing information on local well drilling practices, hydrogeology, and the potential impact of waste constituents on subsurface geochemistry prior to implementation of a ground-water monitoring plan. In this way, maximal benefits will accrue from the considerable outlay of funds, time, and effort involved in subsurface monitoring activities. The most important result may be that in the future we will be in a far better position to effectively manage and protect our ground-water supplies.

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